

JOURNAL AND PROCEEDINGS
OF THE
ROYAL SOCIETY
OF NEW SOUTH WALES

FOR
1949
(INCORPORATED 1881)

VOLUME LXXXIII
Parts I-IV

EDITED BY
W. B. SMITH-WHITE, M.A., B.Sc.
Honorary Editorial Secretary

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† Published September 6, 1950.

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* Published September 26, 1950.

† Published December 6, 1950.

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THE ROYAL SOCIETY of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australasian Philosophical Society", by which title it was known until 1866, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

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Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors," which is obtainable on application to the Honorary Secretaries of the Society.

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Reprints of papers are available.

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P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

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| | | |
|------|------|--|
| 1944 | | Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney. |
| 1938 | P 2 | ‡Albert, Adrien, D.Sc., Ph.D. <i>Lond.</i> , B.Sc. <i>Syd.</i> , A.R.I.C. <i>Gt. B.</i> , Professor of Medical Chemistry, The Australian National University, 183 Euston-road, London N.W.1. |
| 1935 | | ‡Albert, Michael Francois, "Boomerang," Billyard-avenue, Elizabeth Bay. |
| 1898 | | ‡Alexander, Frank Lee, Surveyor, 5 Bennett-street, Neutral Bay. |
| 1941 | | ‡Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W. |
| 1948 | | Anderson, Geoffrey William, B.Sc., 37 Elizabeth-street, Allawah. |
| 1948 | P 1 | Andrews, Paul Burke, Department of Geology, University of Sydney; p.r. 5 Conway-avenue, Rose Bay. |
| 1930 | | Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Camb.</i> , A.M.I.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Rodmyre-road, Strathfield. (President, 1948.) |
| 1919 | P 1 | Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah. |
| 1945 | | Ayscough, Frederick William, B.Sc., 118 Oxford-street, Woollahra. |
| 1935 | | Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown. |
| 1924 | P 2 | Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney. |
| 1934 | P 2 | Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W. |
| 1937 | | Baldick, Kenric James, B.Sc., 19 Beaconsfield-parade, Lindfield. |
| 1946 | P 1 | Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W.; p.r. 78 Alt Street, Ashfield. |
| 1919 | | Bardsley, John Ralph, 76 Wright's-road, Drummoyne. |
| 1947 | | Beckmann, Peter, A.S.T.C., Lecturer in Chemistry, Technical College, Wollongong. |
| 1933 | | Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff. |
| 1926 | | Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble. |
| 1940 | | Betty, Robert Cecil, 67 Imperial-avenue, Bondi. |
| 1937 | P 6 | Birch, Arthur John, M.Sc., D.Phil. (<i>Oxon.</i>), 6 Beechcroft-road, Oxford, England. |
| 1916 | | Birrell, Septimus, 74 Edinburgh-road, Marrickville. |
| 1920 | | Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman. |
| 1939 | P 3 | Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills. |
| 1948 | | Blanks, Fred Roy., B.Sc. (Hons.), Industrial Chemist, 12 Culworth-avenue, Killara. |
| 1946 | | Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carrabella-street, Kirribilli. |
| 1933 | P 29 | Bolliger, Adolph, Ph.D., F.A.C.I., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney. (President, 1945.) |
| 1920 | P 9 | Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., "Hills and Dales," Mittagong. (President, 1935.) |
| 1939 | P 17 | Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c.o. C.S.R. Co. Ltd., Pyrmont; p.r. 41 Spence-road, Killara. |
| 1948 | | Boyd, Eric Harold, B.A., B.Sc., Dip.Ed., F.P.S., The King's School, Parramatta. |

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- 1948 Boyd, Joan, B.Sc. Hons. *Lond.*, Dip.Ed. *Lond.*, The King's School, Parramatta.
 1938 Breckenridge, Marion, B.Sc., Department of Geology, The University of Sydney ;
 p.r. 19 Handley-avenue, Thornleigh.
- 1946 Breyer, Bruno, M.D., Ph.D., M.A., F.A.C.I., Lecturer in Agricultural Chemistry,
 Faculty of Agriculture, University of Sydney, Sydney.
- 1919 P 1 Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of
 Physics, National Standards Laboratory of Australia, University Grounds,
 Sydney ; p.r. 13 Findlay-avenue, Roseville.
- 1942 Brown, Desmond J., M.Sc. (*Syd.*), Ph.D. (*Lond.*), D.I.C., Department of Medical
 Chemistry, Australian National University, 183 Euston-road, London,
 N.W.1.
- 1935 P 7 Browne, Ida Alison, D.Sc., Senior Lecturer in Palaeontology, University of Sydney.
 1945 Brown, Norma Dorothy (Mrs.), B.Sc., Biochemist, 2 Macauley-street, Leich-
 hardt.
- 1941 Brown, Samuel Raymond, A.O.A. *Aust.*, 87 Ashley-street, Chatswood.
 1913, P 22 †Browne, William Rowan, D.Sc., Reader in Geology, University of Sydney.
 (President, 1932.)
- 1947 Buchanan, Gregory Stewart, B.Sc. (Hons.), Lecturer in Physical Chemistry,
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- 1940 Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville.
 1946 Bullen, Keith Edward, M.A., B.Sc. *N.Z.*, M.A. *Melb.*, Ph.D., Sc.D. *Camb.*, F.R.S.,
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 Tasmania.
- 1948 Carroll, Dorothy, B.A., B.Sc., Ph.D., D.I.C., Secretary, Linnean Society of New
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- 1903 P 5 †Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathe-
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 Burradoo, N.S.W.
- 1945 Carter, Harold Burnell, B.V.Sc., Research Officer, C.S.I.R., McMaster
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- 1944 Cavill, George William Kenneth, M.Sc., c/o Department of Organic Chemistry,
 The University, Liverpool, Great Britain.
- 1913 P 4 †Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S. ; p.r. 54 Drum-
 albyn-road, Bellevue Hill. (President, 1933.)
- 1933 Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney.
 1940 Chambers, Maxwell Clark, B.Sc., c/o Coty (England) Ltd., 35-41 Hutchinson-
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- 1913 P 21 †Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.)
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 1938 Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vaucluse.
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 1940 Cohen, Samuel Bernard, M.Sc., A.A.C.I., 8 Roseville-avenue, Roseville.
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 1948 Cole, Leslie Arthur, Company Executive, 21 Carlisle-street, Rose Bay.
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 1946 Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield.
 1920 Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-
 streets, Sydney.
- 1945 Coombes, Arthur Roylance, A.S.T.C. (chem.), 14 Georges River-road, Croydon.
 1913 P 5 †Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney
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- 1933 Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd.,
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- 1937 P 8 Cornforth, Rita Harriet, D.Phil. (*Oxon.*), M.Sc. (*Syd.*), c/o Dyson Perrin's
 Laboratory, South Parks-road, Oxford, England.
- 1940 Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
 1919 Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University
 of Sydney.

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- 1909 P 7 †Cotton, Leo Arthur, M.A., D.Sc., 113 Queen's Parade East, Newport Beach. (President, 1929.)
- 1941 P 1 Craig, David Parker, Lecturer in Inorganic Chemistry, University of Sydney; p.r. 62 Springdale Rd., Killara.
- 1921 P 1 †Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street., Rookdale.
- 1935 P 3 Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
- 1948 Cymerman, John, Ph.D., D.I.C., A.R.C.S., B.Sc., A.R.I.C., Lecturer in Organic Chemistry, University of Sydney.
- 1940 Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
- 1890 †Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
- 1919 P 2 de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
- 1906 †Dixson, Sir William, "Merridong," Gordon-road, Killara.
- 1913 P 3 †Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
- 1928 Donegan, Henry Arthur James, A.S.T.O., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
- 1947 Downes, Alan Marchant, B.Sc. (Hons.), Grandview-avenue, Croydon, Victoria.
- 1948 Doyle, Shirley Kathleen, B.Sc., Microbiologist to H. Jones & Co.; p.r. 74 Duntroon-avenue, Roseville.
- 1943 Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
- 1937 P 13 Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney; p.r. 40 Manning-road, Double Bay. (President, 1947.)
- 1948 Dunlop, Bruce Thomas, B.Sc., Schoolteacher, 77 Stanhope-road, Killara.
- 1924 Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
- 1934 P 40 Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
- 1945 Eade, Ronald Arthur, B.Sc., 21 Steward-street, Leichhardt.
- 1934 P 2 Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
- 1940 Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
- 1937 English, James Roland, L.S., Sydney.
- 1916 P 2 Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
- 1944 Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
- 1908 †Esdaile, Edward William, 42 Hunter-street, Sydney.
- 1935 Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
- 1944 Fairweather, Alwynne Drysdale (Mrs.), B.Sc., 338 Chapple-street, Broken Hill.
- 1909 P 7 †Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
- 1940 Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
- 1940 Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
- 1933 Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
- 1879 †Foreman, Joseph, M.R.C.S. Eng., L.R.C.P. Edin., "The Astor," Macquarie-street, Sydney.
- 1932 Forman, Kenn. P., M.I.Refr.E., 35 Riversdale-road, Hawthorn, Victoria.
- 1905 †Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
- 1940 Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
- 1943 Frederick, Robert Desider Louis, B.E., 162 Buckley-street, Essendon, W.5, Victoria.
- 1940 Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
- 1944 P 2 Friend, James Alan, 16 Kelburn-road, Roseville.
- 1945 Furst, Hellmut Friedrich, B.D.S. (Syd.), D.M.D. (Hamburg), Dental Surgeon, 168 Bellevue-road, Bellevue Hill.
- 1948 Gardiner, Edward Carson, Electrical Engineer in Charge of Construction at the Captain Cook Graving Dock, for the Department of Works and Housing p.r. 39 Spencer-street, Rose Bay.

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| 1935 | P 2 | Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria. |
| 1939 | P 4 | Gascoigne, Robert Mortimer, Chemistry Department, University of Liverpool, England. |
| 1926 | | Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft. |
| 1942 | P 3 | Gibson, Neville Allan, M.Sc., A.R.I.C., Industrial Chemist, 217 Parramatta-road, Haberfield. |
| 1947 | | Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville. |
| 1947 | † | Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville. |
| 1940 | | Gillis, Richard Galvin, Senior Lecturer, Organic Chemistry, Melbourne Technical College; p.r. 4 Tennyson-avenue, Caulfield, S.E.7, Victoria. |
| 1948 | | Glasson, Kenneth Roderick, B.Sc., Geologist, Lake George Mines Ltd., Captain's Flat, N.S.W. |
| 1945 | | Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney. |
| 1947 | | Goldsworthy, Neil Ernest, M.B., Ch.M. Syd., Ph.D., D.T.M. & H. Camb., D.T.M. & H. Eng., D.P.H. Camb., 65 Roseville-avenue, Roseville. |
| 1936 | | Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill. |
| 1948 | | Gray, Charles Alexander Menzies, B.Sc., B.E., 75 Woniara-road, Hurstville. |
| 1938 | | Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe. |
| 1946 | | Gutmann, Felix, Ph.D., F.Inst.P., M.I.R.E., Commonwealth Research Fellow, Faculty of Agriculture, University of Sydney, Sydney. |
| 1948 | | Gyarfas, Eleonora Clara, M.Sc. Budapest, Research Assistant, University of Sydney; p.r. 53 Simpson-street, Bondi. |
| 1947 | | Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney. |
| 1945 | | Hall, Leslie Lionel, Works Chemist, 494 Kent-street, Sydney. |
| 1934 | | Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville. |
| 1892 | † | Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney; p.r. 23 March-street, Bellevue Hill. |
| 1940 | P 14 | Hanlon, Frederick Nool, B.Sc., Geologist, Department of Mines, Sydney. |
| 1905 | P 6 | †Harker, George, D.Sc., F.A.C.I.; p.r. 89 Homebush-road, Strathfield. |
| 1936 | | Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale. |
| 1934 | | Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo. |
| 1948 | P 1 | Harris, Clive Melville, Laboratory Assistant, Museum of Technology and Applied Science; p.r. 12 Livingstone-road, Lidcombe. |
| 1946 | | Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney. |
| 1934 | | Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord; p.r. 34 Nicholson-street, Chatswood. |
| 1919 | | Henriques, Frederick Lester, 208 Clarence-street, Sydney. |
| 1945 | | Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd.; p.r. 10 Cremorne-road, Cremorne. |
| 1938 | P 4 | Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane. |
| 1946 | | Hinder, Nora (Miss), B.Sc. Syd., 22 Chester-street, Epping. |
| 1936 | | Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn. |
| 1928 | | Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood. |
| 1948 | P 3 | Hogarth, Julius William, 8 Jeanneret-avenue, Hunter's Hill. |
| 1916 | | Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, 81 Frederick-street, Rockdale. |
| 1941 | | Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville. |
| 1935 | | Howarth, Mark, F.R.A.S., Grange Mount Observatory, Bull-street, Mayfield, Newcastle, N.S.W. |
| 1938 | P 9 | Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney. |
| 1947 | | Humpoletz, Justin Ernst, B.Sc. Syd., 21 Belgium-avenue, Roseville. |
| 1923 | P 3 | †Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville. |

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| 1943 | | Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville. |
| 1942 | P 1 | Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania. |
| 1946 | | Johnson, Guy Frederick, 644 Botany-road, Alexandria. |
| 1909 | P 15 | Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.) |
| 1935 | P 6 | Joplin, Germaine Anne, B.Sc., Ph.D., Geological Department, University of Sydney; p.r. 18 Wentworth-street, Eastwood. |
| 1948 | P 1 | Jopling, Alan Victor, B.Sc., B.E., 28 Cliff-street, Manly. |
| 1930 | | Judd, William Percy, 123 Wollongong-road, Arncliffe. |
| 1935 | | Kelly, Caroline Tennant (Mrs.), Dip.Anth., "Eight Bells," Cast e Hill. |
| 1940 | | Kennard, William Walter, 9 Bona Vista-avenue, Maroubra. |
| 1924 | P 1 | Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield. |
| 1934 | | Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove. |
| 1948 | | Kimble, Frank Oswald, Engineer, 16 Evelyn-avenue, Concord. |
| 1943 | | Kimble, Jean Annie, B.Sc., Research Chemist, 383 Marrickville-road, Marrickville. |
| 1920 | | Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham. |
| 1948 | | Knight, Oscar Lo Maistro, B.E. Syd., A.M.I.C.E., A.M.I.E.Anst., Engineer, 10 Mildura-street, Killara. |
| 1948 | | Koch, Leo E., Ph.D., D.Sc. (Cologne), Department of Geology, The University of Sydney. |
| 1939 | P 1 | Lamboth, Arthur James, B.Sc., "Naranje," Sweethaven-road, Wetherill Park, N.S.W. |
| 1936 | | Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., Box 21, P.O., Concord. |
| 1946 | | Lederer, Michael, 67 Edgecliff-road, Bondi Junction. |
| 1947 | | Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney. |
| 1936 | P 2 | Lemborg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards. |
| 1920 | | Le Souef, Albert Sherbourne, 3 Silex-road, Mosman. |
| 1929 | P 56 | †Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.) |
| 1942 | | Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney. |
| 1947 | | Lloyd, James Charles, B.Sc. Syd., N.S.W. Geological Survey, 41 Goulburn-street, Liverpool. |
| 1940 | P 1 | Lockwood, William Hutton, B.Sc., F. & A. Inspectorate, 64 H.Q., C.C.G., Minden, Germany. |
| 1906 | | †Loney, Charles Augustus Luxton, M.Am.soc.Refr.E., National Mutual Building, 350 George-street, Sydney. |
| 1947 | | Lowenbein, Gladys Olive (Mrs.), B.Sc. Melb., F.R.I.C. Gt. B., A.A.C.I., Director of Research, Australian Leather Research Association; p.r. "Cahors," No. 75, 117 Macleay-street, Potts Point. |
| 1943 | | †Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park. |
| 1945 | | Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra. |
| 1948 | | Lyons, Lawrence Ernest, B.A., M.Sc., Lecturer in Chemistry, The University of Sydney; p.r. 13 Albert-road, Strathfield. |
| 1942 | | Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, 84 Marine-parade, Maroubra. |
| 1939 | P 4 | Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1. |
| 1943 | | McCoy, William Kevin, Analytical Chemist, c/o Mr. A. J. McCoy, 39 Malvern-avenue, Merrylands. |
| 1940 | | McGrath, Brian James, 40 Mooramie-avenue, Kensington. |
| 1940 | | McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills. |
| 1948 | | McInnes, Gordon Elliott, Department of Geology, The University of Sydney; p.r. 46 Laycock-street, Bexley. |

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| 1906 | P 2 | †McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville. |
| 1891 | P 1 | †McKay, R. T., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney. |
| 1944 | P 7 | McKenzie, Hugh Albert, B.Sc., c/o Frick Chemical Laboratory, Princeton University, Princeton, New Jersey, U.S.A. |
| 1943 | | McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo; p.r. Flat 2, 42A, Waimea-street, Burwood. |
| 1947 | | McMahon, Patrick Reginald, M.Agr.sc. N.Z., Ph.D. Leeds, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney. |
| 1927 | | McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W. |
| 1943 | | McNamara, Barbara Joyce (Mrs.), M.B., B.S., Yeoval, 7.W. |
| 1946 | | McPherson, John Charters, 14 Sarnar-road, Greenwich. |
| 1946 | P 1 | McRoberts, Helen May, B.Sc., New England University College, Armidale. |
| 1947 | | Magee, Charles Joseph, D.Sc.Agr. Syd., M.Sc. Wis., Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville. |
| 1947 | | Maley, Leo Edmund, M.Sc., B.Sc. (Hons.), A.A.C.I., A.M.A.I.M.M., 116 Maitland road, Mayfield. |
| 1940 | | Malone, Edward E., 33 Windsor-road, St. Mary's. |
| 1947 | P 8 | Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W. |
| 1944 | | Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield. |
| 1946 | | May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill. |
| 1935 | P 1 | Maze, Wilson Harold, M.Sc., Deputy Registrar, University of Sydney, Sydney. |
| 1912 | | †Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly. |
| 1929 | P 25 | Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.) |
| 1941 | | Melville, George Livingstone, Managing Director, Federal Machine Co. Ltd., Loftus-street, Arncliffe. |
| 1928 | | Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, "Walla Walla," Hull-road, Beecroft. |
| 1940 | | Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd. 15 Shaw-avenue, Earlwood. |
| 1941 | | Morrissey, Matthew John, B.A., A.S.T.C., Auburn-street, Parramatta. |
| 1922 | P 28 | Morrison, Frank Richard, A.A.C.I., F.C.S., Deputy Director, Museum of Technology and Applied Science, Harris-street, Ultimo. |
| 1934 | | Mort, Francis George Arnot, A.A.C.I., Chemist, 16 Grafton-street, Woollahra. |
| 1948 | | Mosher, Kenneth George, B.Sc., Geologist, Geological Survey, Department of Mines, Bridge-street, Sydney. |
| 1944 | | Moye, Daniel George, B.Sc., Geologist, Warragamba Dam. |
| 1946 | | Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney. |
| 1948 | | Mulley, Joan W., Technical Officer, C.S.I.R.; p.r. 4 Billyard-avenue, Elizabeth Bay. |
| 1915 | | Murphy, Robert Kenneth, Dr.Eng., Chem., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney. |
| 1923 | P 2 | Murray, Colonel Jack Keith, B.A., B.Sc.Agr., Administrator, Territory of Papua-New Guinea, Government House, Port Moresby. |
| 1948 | | Naylor, Betty Yvonne, B.Sc., 6 Niblick-avenue, Roseville. |
| 1930 | P 6 | Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.L.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld. |
| 1943 | | Neuhaus, John William George, 190 Old Prospect-road, Wentworthville. |
| 1932 | | Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Professor of Botany, The University of Ceylon, Colombo, Ceylon. |
| 1943 | | Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. No. 2 Flat, corner Hendy-avenue and Rainbow-streets, Coogee. |
| 1935 | | Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown. |
| 1945 | P 1 | Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T. |
| 1938 | P 1 | Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic. |
| 1920 | P 4 | †Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.) |

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| 1947 | | Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 1 Edgecliff-road, Bondi Junction. |
| 1948 | | Northcott, Jean, B.Sc. (Hons.), Chemistry Department, The University of Sydney; p.r. 38 Canberra-street, Lane Cove. |
| 1940 | P 25 | Nyholm, Ronald Sydney, M.Sc., Chemistry Department, University College, Gower-street, London, W.C.1, England. |
| 1935 | P 4 | O'Connell, Rev. Daniel J. K., S.J., M.Sc., D.Ph., F.R.A.S., Riverview College Observatory, Sydney. |
| 1947 | | Old, Adrian Noel, B.Sc. Agr., Chemist, Department of Agriculture; p.r. 4 Springfield-avenue, Pott's Point. |
| 1921 | P 10 | Osborne, George Davenport, D.Sc. Syd., Ph.D. Camb., Senior Lecturer in Geology in the University of Sydney. (President, 1944.) |
| 1920 | P 75 | Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.) |
| 1948 | | Perry, Hubert Roy, B.Sc., 74 Woodbine-street, Bowral. |
| 1938 | | Phillips, Marie Elizabeth, B.Sc., 4 Morella-road, Clifton Gardens. |
| 1935 | | Phillips, Orwell, 55 Darling Point-road, Edgecliff. |
| 1946 | | Pinwell, Norman, B.A. (Q'land), The Scots College, Bellevue Hill. |
| 1943 | | Plowman, Ronald Arthur, A.S.T.C., A.A.C.I., Analytical Chemist, 78 Alt-street, Ashfield. |
| 1919 | | Poate, Hugh Raymond Guy, M.B., Ch.M. Syd., F.R.C.S. Eng., L.R.C.P. Lond., F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill. |
| 1896 | | †Pope, Roland James, B.A. Syd., M.D., Ch.M., F.R.C.S. Edin., 185 Macquarie-street, Sydney. |
| 1946 | | Potter, Bryco Harrison, B.Sc. (Hons.) (Syd.), 13 Fuller's-road, Chatswood. |
| 1921 | P 2 | Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman. |
| 1938 | | Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern. |
| 1945 | | Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst. |
| 1927 | | Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara. |
| 1918 | P 1 | Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney. (President, 1942-43.) |
| 1945 | | Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood. |
| 1893 | | †Purser, Cecil, B.A., M.B., Ch.M. Syd., "Ascot," Grosvenor-road, Wahroonga. |
| 1935 | P 3 | †Quodling, Florrie Mabel, B.Sc., Lecturer in Geology, University of Sydney |
| 1922 | P 6 | Raggatt, Harold George, D.Sc., Director, Mineral Resources Survey, Department of Supply, Canberra, A.C.T. |
| 1940 | P 2 | Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping. |
| 1919 | P 3 | Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., 57 William-street, Sydney. |
| 1936 | | Randall, Harry, Buena Vista-avenue, Denistone. |
| 1947 | | Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield. |
| 1947 | | Ray, Reginald John, Plastics Manufacturer and Research Chemist, 14 Hedger-avenue, Ashfield. |
| 1931 | P 1 | Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, Vic. |
| 1935 | | Reid, Cicero Augustus, 19 Newton-road, Strathfield. |
| 1947 | | Reuter, Fritz Henry, Ph.D. (Berlin, 1930), F.A.C.I., 94 Onslow-street, Rose Bay. |
| 1946 | | Rhodes-Smith, Cecil, 261 George-street, Sydney. |
| 1947 | | Ritchie, Arthur Sinclair, A.S.T.C., Lecturer in Mineralogy and Geology, Newcastle Technical College; p.r. 188 St. James-road, New Lambton, N.S.W. |
| 1947 | | Ritchie, Bruce, B.Sc. (Hons.), c/o Pyco Products Pty. Ltd., 576 Parramatta-road, Petersham. |
| 1939 | P 16 | Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney. |
| 1939 | P 3 | Robbins, Elizabeth Marie (Mrs.), M.Sc., 344 Railway-parade, Guildford. |

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| 1933 | | Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney. |
| 1940 | | Robertson, Rutherford Ness, B.Sc. <i>Syd.</i> , Ph.D. <i>Cantab.</i> , Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale. |
| 1935 | P 2 | Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney. |
| 1940 | | Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick. |
| 1948 | | Rosenthal-Schneider, Ilse, Ph.D., 48 Cambridge-avenue, Vacluse. |
| 1940 | | Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield. |
| 1948 | | Ross, Leonard Paul, B.Sc., 137 Burwood-road, Enfield. |
| 1945 | | Rountree, Phyllis Margaret, M.Sc. <i>Melb.</i> , Dip.Bact. <i>Lond.</i> , Royal Prince Alfred Hospital, Sydney. |
| 1945 | | Sambell, Pauline Mary, B.A. (Zoology), Assistant Research Officer, McMaster Laboratory; p.r. 83 Woniora-road, Hurstville. |
| 1945 | | Sampson, Aileen (Mrs.), Sc.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping. |
| 1941 | P 3 | Sawkins, Dansie Thomas, M.A. <i>Syd.</i> , B.A. <i>Camb.</i> , 60 Boundary-street, Roseville. |
| 1920 | | Scammell, Rupert Boswood, B.Sc. <i>Syd.</i> , A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens. |
| 1948 | P 1 | Schafer, Harry Neil Scott, B.Sc., 18 Bartlett-street, Summer Hill. |
| 1946 | P 1 | Scott, Beryl (Miss), B.Sc., Geology Department, University of Tasmania. |
| 1940 | | Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria. |
| 1933 | | Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney. |
| 1936 | | Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A. |
| 1948 | | Sharp, Kenneth Raeburn, Geology Department, The University of Sydney; p.r. Kitchener-road, St. Ives. |
| 1938 | | Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, c/o Shell Co. of Aust., North Terrace, Adelaide. |
| 1936 | P 2 | Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. <i>Melb.</i> , 43 Robertson-road, Centennial Park. |
| 1948 | | Sherwood, Ian Russell, D.Sc., F.A.C.I., Research Bacteriologist, Research Laboratory, Colonial Sugar Refining Co. Ltd., John-street, Pyrmont. |
| 1945 | | Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra. |
| 1945 | P 2 | Simmons, Lewis Michael, B.Sc. (Hons.) <i>Lond.</i> , Ph.D. <i>Lond.</i> , F.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill. |
| 1948 | | Simonett, David Stanley, B.Sc., Geography Department, The University of Sydney; p.r. 14 Selwyn-street, Artarmon. |
| 1943 | | Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill. |
| 1933 | | Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiatea," Oyama-avenue, Manly. |
| 1940 | | Smith, Eric Brian Jeffcoat, New College, Oxford, England. |
| 1947 | | Smith-White, William Broderick, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , Department of Mathematics, University of Sydney; p.r. 7 Henson-street, Summer Hill. |
| 1919 | | Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W. |
| 1921 | | Spencer-Watts, Arthur, "Araboono," Glebe-street, Randwick. |
| 1916 | | Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney. |
| 1914 | | †Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vacluse. |
| 1948 | P 1 | Stevens, Neville Cecil, B.Sc., Geology Department, The University of Sydney; p.r. 12 Salisbury-street, Hurstville. |
| 1900 | P 1 | †Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berele," Homebush-road, Strathfield. (President, 1927.) |
| 1942 | | Still, Jack Leslie, B.Sc., Ph.D., Department of Biochemistry, The University, Sydney. |
| 1916 | P 1 | Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney; p.r. 79 Ocean-street, Woollahra. |
| 1918 | | †Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield. |

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| 1919 | | †Sutherland, George Fife, A.R.C.Sc. <i>Lond.</i> , Assistant Professor of Mechanical Engineering in the University of Sydney. |
| 1920 | | Sutton, Harvey, O.B.E., M.D., D.P.H. <i>Melb.</i> , B.Sc. <i>Oxon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay. |
| 1941 | P 2 | Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , c/o Technical Service Department, Iclanz, Box 1911, G.P.O., Melbourne, Victoria. |
| 1948 | | Swinbourne, Ellice Simmons, Organic Chemist, 183 Sydney-road, Balgowlah. |
| 1915 | P 3 | Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville. |
| 1944 | | Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P., 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic. |
| 1946 | | Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A. |
| 1919 | | Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft. |
| 1935 | | Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland. |
| 1923 | | Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham. |
| 1940 | | Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay. |
| 1943 | | Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman. |
| 1921 | | Vicars, Robert, Marrickville Woollen Mills, Marrickville. |
| 1935 | | Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham. |
| 1933 | P 5 | Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale. |
| 1903 | P 10 | †Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.) |
| 1948 | | Walker, Donald Francis, Surveyor, 13 Beauchamp-avenue, Chatswood. |
| 1943 | | Walker, James Foote, Company Secretary, 11 Bruce-dale-avenue, Epping. |
| 1919 | P 2 | Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.) |
| 1913 | P 5 | †Wardlaw, Hy. Sloane Halcro, D.Sc. <i>Syd.</i> , F.A.C.I., Lecturer and Demonstrator in Biochemistry in the University of Sydney. (President, 1939.) |
| 1944 | | Warnor, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T. |
| 1921 | | †Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett, Illoura-avenue, Wahroonga. |
| 1919 | P 1 | Waterhouse, Lionel Lawry, B.E. <i>Syd.</i> , Reader in Geology in the University of Sydney. |
| 1919 | P 7 | Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.) |
| 1944 | | Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney. |
| 1911 | P 1 | †Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.) |
| 1947 | | Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930) Pty. Ltd., 99 York-street, Sydney. |
| 1921 | | Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney. |
| 1947 | | Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick. |
| 1946 | | Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill. |
| 1909 | P 3 | †White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown. |
| 1943 | | Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney. |
| 1928 | | Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield. |
| 1942 | | Williams, Gordon Roy, B.Sc., 45 Conder-street, Burwood. |

Elected.

| | | |
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| 1945 | | Willis, Jack Lehane, B.Sc., Flat 5, "Narooma", Hampden-street, North Sydney. |
| 1943 | | Winch, Leonard, B.Sc., 60 Baldwin-avenue, Asquith. |
| 1940 | | Wogan, Samuel James, Range-road, Sarina, North Queensland. |
| 1936 | P 7 | Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer, Sydney Observatory, Sydney. |
| 1906 | P 12 | †Woolnough, Walter George, D.Sc., F.G.S., c/o Mr. W. L. Woolnough, "Callabonna", 8 Park-avenue, Gordon. |
| 1916 | | Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 7 Wynyard-street, Sydney. |
| 1946 | | Wyndham, Norman Richard, M.D., M.S. (Syd.), F.R.C.S. (Eng.), F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney. |
| 1948 | | Zingel, Judith, B.Sc., Geology Department, The University of Sydney; p.r. 89 Sydney-road, Manly. |

HONORARY MEMBERS.*Limited to Twenty.***Elected.**

| | | |
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| 1949 | | Burnet, Frank Macfarlane, M.D., Ph.D., F.R.S., Director of the Walter and Eliza Hall Research Institute, Melbourne. |
| 1949 | | Florey, Sir Howard, M.B., B.S., B.Sc., M.A., Ph.D., F.R.S., Professor of Pathology, Oxford University, England. |
| 1914 | | Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England. |
| 1946 | | Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E.10. |
| 1915 | | Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A. |
| 1912 | | Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England. |
| 1948 | | Oliphant, Marcus L., B.Sc., Ph.D., F.R.S., Professor of Physics, The University Edgbaston, Birmingham 15, England. |
| 1948 | | Robinson, Sir Robert, M.A., D.Sc., F.C.S., F.I.C., F.R.S., Professor of Chemistry Oxford University, England. |
| 1946 | | Wood-Jones, F., D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (Lond.), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England. |

OBITUARY, 1948-49.

- 1909 Ernest Clayton Andrews.
 1923 George Frederick Birks.
 1932 Ernest Norman McKie.
 1920 Edward Montague Wellish.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
"The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
"Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
"The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flott, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers, D.Sc.
1948. "The Sedimentary Succession of the Bibliando Dome: Record of a Prolonger Proterozoic Ice Age." By Sir Douglas Mawson, O.B.E., F.R.S., D.Sc., B.E.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.

- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
 1886 *Professor L. G. De Koninck, M.D.
 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
 1893 *Professor Ralph Tate, F.L.S., F.G.S.
 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
 1895 *Robert Etheridge, Jnr.
 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
 1901 *Edward John Eyre.
 1902 *F. Manson Bailey, C.M.G., F.L.S.
 1903 *Alfred William Howitt, D.Sc., F.G.S.
 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
 1909 *Dr. Walter E. Roth, B.A.
 1912 *W. H. Twelvetroes, F.G.S.
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
 1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
 1920 *Joseph Edmund Carne, F.G.S.
 1921 *Joseph James Fletcher, M.A., B.Sc.
 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
 1925 *Charles Hedley, F.L.S.
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
 1928 Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
 1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
 1935 *George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
 1938 *Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
 1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.
 1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
 1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.
 1947 *Hubert Lyman Clark, A.B. D.Sc., Ph.D., Hancock Foundation, U.S.C., Los Angeles, California.
 1948 Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney.

AWARDS OF THE JAMES COOK MEDAL.

Bronze Medal.

Awarded annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

- 1947 Smuts, Field-Marshal The Rt. Hon. J. C., P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor, University of Capetown, South Africa.
 1948 Houssay, Bernardo A., Professor of Physiology, Instituto de Biología y Medicina Experimental, Buenos Aires, Argentina.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
 1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.
 1948 Waterhouse, Walter L., M.S., D.Sc.Agr., D.I.C., F.L.S., Sydney, in recognition of his valuable contributions in the field of agricultural research.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £75.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past six years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
 1932 Charles Halliboy Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.
 1938 Frank Macfarlane Burnet, M.D. (Melb.), Ph.D. (Lond.), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
 1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
1940 G. J. Burrows, B.Sc., University of Sydney.
1942 J. S. Anderson, B.Sc., Ph.D. (Lond.), A.R.C.S., D.I.C., University of Melbourne.
1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
1946 Briggs, L. H., D.Phil. (Oxon.), D.Sc. (N.Z.), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
1948 Ian Lauder, M.Sc., Ph.D., University of Queensland, Brisbane.

Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1949.

PRESENTED AT THE ANNUAL GENERAL MEETING OF THE SOCIETY, 6TH APRIL, 1949

(RULE XXVI).

The membership of the Society at the end of the period under review stood at 354. Thirty-eight new members were elected during the year, the Council having made a special effort towards increased enrolment; however, twelve members were lost by resignation and four, who were in arrears with subscriptions, were removed from the register. Four members have been lost to the Society by death since 1st April, 1948:

Ernest Clayton Andrews (1909).

George Frederick Birks (1923).

Ernest Norman McKie (1932).

Edward Montague Wellish (1920).

Professor Marcus L. Oliphant, B.Sc., Ph.D., F.R.S., and Professor Sir Robert Robinson, M.A., D.Sc., F.C.S., F.I.C., F.R.S., were elected to honorary membership of the Society at the annual meeting on 7th April, 1948.

During the year nine general monthly meetings were held, at which the average attendance was 49. Thirty-nine papers were accepted for reading and publication by the Society, an increase of four from the previous year.

At the annual and general monthly meeting of 7th April, 1948, the Acting President, Dr. F. Lions, welcomed Professor Griffith Taylor, of the University of Toronto, Canada, formerly of Sydney University. Professor Taylor gave an address describing the application of geography, geology and physiography to national planning.

The Council decided to devote portion of the time of general meetings to "Notes, Exhibits and Questions". This seems to have met with success, and the following questions have been answered:

4th August:

"There is evidence that ice ages have occurred simultaneously in both hemispheres of the world—what is the evidence of this?" Answered by Dr. G. D. Osborne.

"What is a Transcendental Number?" Answered by Mr. W. B. Smith-White.

"What are Cosmic Rays?" Answered by Dr. R. E. B. Makinson.

6th October:

"Why are there black and white races?" Answered by Professor A. P. Elkin.

"Why does the moon always turn the same face towards the earth?" Answered by Mr. Harley Wood.

1st December:

"What is the principle of the electron microscope?" Answered by Mr. R. L. Werner.

"What was the cause of the change of longitude of Sydney Observatory amounting to some 166 yards in about the year 1932, as indicated by certain one-inch military maps?" Answered by Mr. Harley Wood.

Exhibits discussed were:

5th May:

"Bouncing Putty", by Dr. D. P. Mellor.

3rd June:

"Enlarged photographs of the Second Positive Spectrum of Nitrogen, showing some features of interest", by Professor O. U. Vonwiller and Miss D. P. Tarrant.

A symposium on the "Education of a Scientist" was held at the general monthly meeting on 1st September, the following addresses being given:

"Science in Secondary Education", by Mr. J. B. Thornton.

"The Teaching of Science in the Universities", by Professor N. A. Burges.

"The Scientist and Scientific Method", by Professor K. E. Bullen.

The topic stimulated a deal of discussion, which was continued by other speakers at the next general meeting.

Addresses commemorating great scientists and important scientific events were given at the general monthly meeting on 3rd November:

"Simon Stevin" (Stevinus), by Mr. H. H. Thorne.

"Berzelius", by Mr. J. B. Thornton.

"Important Events in the History of Public Health", by Professor Harvey Sutton.

In continuance of its programme of popular education as to atomic energy, the Society made arrangements with the University Extension Board for the delivery of a series of lectures on atomic physics during July:

"The Atom and Radioactivity", by Dr. D. P. Mellor.

"Artificial Transformations and Nuclear Fission", by Dr. R. E. B. Makinson.

"Atomic Physics and Human Welfare", by Dr. F. Lions.

"International Control of Atomic Energy", by Dr. G. H. Briggs.

Four Popular Science Lectures were delivered during the year, and much appreciated by members of the Society and the public:

20th May: "The Struggle between Fungi and Roots", by Professor N. A. Burges.

17th June: "Plant Growth Regulators or Hormones", by Dr. C. J. Magee.

16th September: "The Making of an Australian—A Study in Migration", by Mrs. C. Kelly.

21st October: "Weights and Measures", by Mr. N. A. Esserman.

A visit to the National Standards and Radiophysics Laboratories on 30th July was arranged through the courtesy of the C.S.I.R. The opportunity to see the work in progress in these laboratories was appreciated by members.

The Annual Dinner of the Society was held at the Sydney University Union on 31st March, 1949. There were present 98 members and friends.

The Section of Geology, whose chairman was Mr. C. St. J. Mulholland and honorary secretary Mr. R. O. Chalmers, held six meetings during the year, at which the average attendance was fourteen members and six visitors. The activities were:

16th April: Address by Mr. F. N. Hanlon.

21st May: Notes and Exhibits by Miss F. Quodling and Messrs. N. C. Stevens, C. St. J. Mulholland, H. O. Fletcher and R. O. Chalmers.

23rd July: Exhibit by Mrs. K. Sherrard and an address by Dr. L. E. Koch.

27th August: Address by Dr. J. A. Dulhunty.

17th September: Address by Dr. G. D. Osborne and Mr. P. B. Andrews.

19th November: Address by Dr. L. E. Koch.

The Council of the Society held ten ordinary meetings and one special meeting during the year, at which the average attendance was 13. The special meeting of the Council was held to discuss the "Freedom of Science". It was resolved that at the time no action beyond remaining vigilant appeared desirable, but a motion defining the Council's attitude was recorded in the minute book.

The Council has decided that in future the Annual Report, Financial Statement and List of Members will be published in Part I of the Journal, and that the abstract of proceedings of meetings will be omitted. This will effect more prompt publication of the reports and eliminate some duplication.

Professor O. U. Vonwiller and the Rev. D. J. K. O'Connell were given leave for periods of travel abroad. Among other activities, they represented Australian Science at the Zurich meeting of the International Astronomical Union. Professor Vonwiller represented the Society at the celebration in Sweden of the one hundredth anniversary of the death of Jacob Berzelius. Mr. W. B. Smith-White was elected to the office of Honorary Editorial Secretary rendered vacant by the resignation of Professor Vonwiller.

The President, Dr. R. L. Aston, has represented the Royal Societies of Australia on the National Co-operating Body in Natural Sciences of UNESCO. At the A.N.Z.A.A.S. Conference, January, 1949, at Hobart, the Society was represented by Drs. R. L. Aston, A. Bolliger and C. J. Magee. At the Seventh Pacific Science Congress, which was held in New Zealand, February, 1949, the Society was represented by Dr. Dorothy Carroll.

Dr. A. B. Walkom was one of Australia's representatives at the General Assembly of UNESCO at Beirut, and was president of the Hobart meeting of the Australian and New Zealand Association for the Advancement of Science in January, 1949.

Professor K. E. Bullen has been elected as a Fellow of the Royal Society.

On Science House Management Committee the Society was represented by Messrs. H. O. Fletcher and F. R. Morrison, with substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

Science House Extension Committee has been working on the proposals for the eventual extension of Science House to York Street North, the representatives of the Royal Society of New South Wales being Drs. A. Bolliger and R. L. Aston.

The Clarke Memorial Lecture for 1948 was delivered by Sir Douglas Mawson, O.B.E., D.Sc., F.R.S., on 15th July, the title being "The Sedimentary Succession of the Bibliando Dome: Record of a Prolonged Proterozoic Ice Age".

The Liversidge Research Lecture for 1948 was delivered by Professor Ian Lauder, M.Sc., Ph.D., on 19th August, on "Some Recent Work on the Separation and Use of Stable Isotopes".

The Clarke Memorial Medal for 1948 was awarded to Dr. Arthur B. Walkom, Director, Australian Museum, Sydney, in recognition of his contributions to natural science, and particularly for researches in paleobotany.

The Clarke Memorial Medal for 1949 was awarded to the Rev. H. Montague Rupp for his work on Australian orchids.

The Royal Society's Medal was awarded to Professor W. L. Waterhouse, M.C., D.Sc.Agr., D.I.C., F.L.S., in recognition of his valuable researches in the field of agriculture.

The James Cook Medal was awarded to Professor Bernado A. Houssay, of the Instituto d Biologia y Medicina Experimental, Buenos Aires, Argentina, for his distinguished work for science and human welfare in the southern hemisphere, particularly through his contributions to endocrine research.

The Edgeworth David Medal, which is for Australian research workers under thirty-five years of age, was awarded for the first time. It was decided to make a joint award to Mr. R. G. Giovanelli, M.Sc., for his work in astrophysics, and Mr. E. Ritchie, M.Sc., for his work in organic chemistry.

The initiation of the James Cook Medal, in 1948, and the Edgeworth David Medal completes the scheme of the Society's awards which has been envisaged in recent years.

During the year several scientists from overseas visited the Society's rooms and were entertained by the President. Among these were:

Sir Harold Hartley, now Chairman of the British Overseas Airways Corporation (23rd November, 1948).

Sir Henry Tizard, who visited Australia at the invitation of the Commonwealth Government to advise on defence research (8th December, 1948).

Dr. Wang Ghing-Hsi, senior member of the Natural Sciences Department, UNESCO Secretariat, Paris (28th February, 1949).

Drs. A. Sison, P. Valenzuela and J. M. Feliciano, who were members of a party of Philipino scientists returning from the Seventh Pacific Science Congress in New Zealand (14th February, 1949).

Dr. S. Krishna, Lt.-Col. M. L. Ahuja, Dr. B. P. Pal and Mr. V. P. Sondhi, who were members of an Indian scientific delegation visiting Australia at the invitation of the Commonwealth Government (28th March, 1949).

The financial position of the Society, as disclosed by the annual audit, reveals the difficulties which in these years beset institutions whose income tends to remain steady but whose expenditure continues to increase obstinately despite efforts at economy which, if the tendency continues, may eventually affect the efficiency of the Society's work. The most serious example of rising costs for us is in the cost of printing the Journal and Proceedings, which in 1947 was increased from £13 to £16 per forme of 16 pages; we are now faced with an increase to £32.

The Royal Society's share of the profits of Science House for the year was £390 18s. 6d.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of our Society is much appreciated.

The Library. The amount of £58 6s. 3d. has been spent on the purchase of periodicals, and £121 11s. 3d. on binding, the increased expenditure on binding being due to shortage of book-binding materials in 1947-1948.

Exchange of publications is maintained with 406 societies and institutions, an increase of 19 over the previous year.

The number of accessions entered in the catalogue during the year ended 28th February, 1949, was 2,501 parts of periodicals.

The Society sold its set of the *Journal of the Royal Asiatic Society of Great Britain and Ireland* to the Library, the Parliament of the Commonwealth, for the sum of £222 12s. 6d. Also, incomplete sets of medical journals were sold to Stechert-Hafner, Inc., of New York, and realized the sum of £202 5s. 11d.

Among the institutions which made use of our library through the inter-library borrowing scheme were: The University of Sydney, Department of Health, University of Queensland, Commonwealth Observatory, C.S.I.R. Food Preservation, Linnean Society of N.S.W., Forestry Commission, C.S.I.R. Plant Industry, National Standards Laboratories, M.W.S. and D. Board, McMaster Laboratory, Taubman's Paints, Elliotts and Australian Drug Co. Ltd., A.W.A. Ltd., C.S.I.R. Industrial Chemistry, Department of Agriculture, Defence Research Laboratories, Water Conservation and Irrigation Commission, Australian Paper Mills, Sydney Technical College, the University of Melbourne, Colonial Sugar Refining Co. Ltd., C.S.I.R. Aeronautics, Standards Association of Australia, C.S.I.R. Coal Survey, Sydney Grammar School, the Australian Museum, Institute of Engineers, James Hardie & Co.

R. L. ASTON,
President.

THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 28th FEBRUARY, 1949.

LIABILITIES.

| 1948. | | | | 1949. | | | |
|---------|--|--|--|-------|----|----|--------------|
| £ | | | | £ | s. | d. | £ s. d. |
| 189 | Accrued Expenses | | | | | | 141 5 9 |
| 25 | Subscriptions Paid in Advance | | | | | | 26 5 0 |
| | Life Members' Subscriptions—Amount carried forward | | | | | | 90 0 0 |
| | James Cook and Edgeworth David Medals—Amount carried forward | | | | | | — |
| 200 | Trust and Monograph Capital Funds (detailed below)— | | | | | | |
| | Clarke Memorial | | | 1,960 | 4 | 7 | |
| | Walter Burfitt Prize | | | 1,055 | 17 | 5 | |
| | Liversidge Bequest | | | 707 | 10 | 3 | |
| 7,173 | Monograph Capital Fund | | | 3,520 | 18 | 4 | |
| | | | | | | | 7,244 10 7 |
| 25,877 | ACCUMULATED FUNDS | | | | | | 26,081 18 2 |
| (902) | Contingent Liability—In connection with tenancies of the Australian National Research Council and the Pharmaceutical Society of N.S.W.—Maximum Liability £901 16s. 8d. | | | | | | |
| £33,566 | | | | | | | £33,583 19 6 |

ASSETS.

| 1948. | | | | 1949. | | | |
|---------|---|--|--|-------|----|----|--------------|
| £ | | | | £ | s. | d. | £ s. d. |
| 596 | Cash at Bank and in Hand | | | | | | 439 14 3 |
| | Investments—Commonwealth Bonds and Inscribed Stock, etc.—at Face Value— | | | | | | |
| | Held for— | | | | | | |
| | Clarke Memorial Fund | | | 1,800 | 0 | 0 | |
| | Walter Burfitt Prize Fund | | | 1,000 | 0 | 0 | |
| | Liversidge Bequest | | | 700 | 0 | 0 | |
| | Monograph Capital Fund | | | 3,000 | 0 | 0 | |
| | General Purposes | | | 4,660 | 0 | 0 | |
| 10,860 | | | | | | | 11,160 0 0 |
| 161 | Prepayment | | | | | | 24 2 9 |
| | Debtors for Subscriptions | | | 85 | 5 | 0 | |
| | Deduct Reserve for Bad Debts | | | 85 | 5 | 0 | |
| | | | | | | | — |
| 14,715 | Science House—One-third Capital Cost | | | | | | 14,745 18 6 |
| 6,800 | Library—At Valuation | | | | | | 6,800 0 0 |
| 396 | Furniture—At Cost—less Depreciation | | | | | | 379 0 0 |
| 29 | Pictures—At Cost—less Depreciation | | | | | | 27 4 0 |
| 9 | Lantern—At Cost—less Depreciation | | | | | | 8 0 0 |
| £33,566 | | | | | | | £33,583 19 6 |

TRUST AND MONOGRAPH CAPITAL FUNDS.

| | Clarke Memorial. £ s. d. | Walter Burfitt Prize. £ s. d. | Liversidge Bequest. £ s. d. | Monograph Capital Fund. £ s. d. |
|-----------------------------------|--------------------------------|--|-----------------------------------|--|
| Capital at 29th February, 1948 .. | 1,800 0 0 | 1,000 0 0 | 700 0 0 | 3,000 0 0 |
| Revenue— | | | | |
| Balance at 29th February, 1948 | 128 3 8 | 97 7 10 | 25 15 0 | 421 13 4 |
| Interest for twelve months .. | 64 13 11 | 34 15 0 | 25 15 0 | 99 5 0 |
| | 192 17 7 | 132 2 10 | 51 10 0 | 520 18 4 |
| Deduct Expenditure .. | 32 13 0 | 76 5 5 | 43 19 9 | — |
| Balance at 28th February, 1949 .. | £160 4 7 | £55 17 5 | £7 10 3 | £520 18 4 |

ACCUMULATED FUNDS.

| | £ | s. | d. |
|--|--------|---------|------|
| Balance at 29th February, 1948 | 25,877 | 0 | 11 |
| Add— | | | |
| Surplus for twelve months (as shown by Income and Expenditure Account) | £227 | 10 | 6 |
| Decrease in Reserve for Bad Debts | 32 | 7 | 0 |
| | | 259 | 17 6 |
| | | 26,136 | 18 5 |
| Less— | | | |
| Amount written off <i>re</i> James Cook and Edgeworth David Medals | 4 | 12 | 0 |
| Bad Debts written off | 50 | 8 | 3 |
| | | 55 | 0 3 |
| | | £26,081 | 18 2 |

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1949, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Chartered Accountants (Aust.).

Prudential Building,
39 Martin Place,
Sydney, 24th March, 1949.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1948, to 28th February, 1949.

| 1947-8. | | 1948-9. | |
|---------|---|-------------|---------|
| £ | | £ s. d. | £ s. d. |
| 507 | To Printing and Binding Journal—Vol. 81 | 639 13 4 | |
| 362 | „ Salaries | 467 15 1 | |
| 150 | „ Library—Purchases and Binding | 133 6 3 | |
| 90 | „ Printing—General | 103 9 2 | |
| 127 | „ Miscellaneous | 96 11 5 | |
| 95 | „ Postage and Telegrams | 74 0 10 | |
| 46 | „ Rent—Science House Management Committee .. | 54 18 5 | |
| 37 | „ Cleaning | 37 0 0 | |
| 23 | „ Depreciation | 22 16 7 | |
| 19 | „ Telephone | 22 3 7 | |
| 15 | „ Insurance | 23 11 0 | |
| 19 | „ Audit | 18 18 0 | |
| 12 | „ Electricity | 8 18 2 | |
| 18 | „ Repairs | 1 19 6 | |
| | „ Reprints— | | |
| | Expenditure £153 18 2 | | |
| | Less Received 97 9 0 | | |
| 116 | | 56 9 2 | |
| | „ Annual Dinner— | | |
| | Expenditure £88 13 6 | | |
| | Less Received 49 16 0 | | |
| 21 | | 38 17 6 | |
| 31 | „ Conversazione | — | |
| 1,688 | | 1,800 8 0 | |
| — | „ Surplus for Twelve Months | 227 10 6 | |
| £1,688 | | £2,027 18 6 | |
| 1947-8. | | 1948-9. | |
| £ | | £ s. d. | |
| 557 | By Membership Subscriptions | 586 8 6 | |
| 400 | „ Government Subsidy | 400 0 0 | |
| 482 | „ Science House—Share of Surplus | 390 18 6 | |
| 157 | „ Interest on General Investments | 155 12 1 | |
| — | „ Proceeds Sale of Old Library Books | 477 18 7 | |
| — | „ Other Receipts | 5 0 10 | |
| 10 | „ Proportion of Life Members' Subscriptions | 12 0 0 | |
| 82 | „ Deficit for Twelve Months | — | |
| £1,688 | | £2,027 18 6 | |

Obituary.

ERNEST CLAYTON ANDREWS died July 1st, 1948. He was born in 1870 and had occupied a distinguished position in Australian Science for many years. He became a member of the Royal Society of New South Wales in 1909 and was a member of its Council from 1917 to 1932 except in 1919 and in 1927, during the latter of which he was invited to the United States of America to deliver the Silliman Lectures at Yale University. He was president of the Society in 1921 and was awarded the Clarke Memorial Medal in 1928 and the Clarke Memorial Lectureship in 1942.

Andrews was a graduate of the School of Geology of Sydney University, under Professor David, and joined the Geological Survey of New South Wales in 1899, becoming Government Geologist in 1920. His many published papers, twelve of them in the *Journal and Proceedings* of the Society, show a grasp of a wide variety of geological subjects, but reveal his special insight into the principles governing the evolution of physiographic features and their relation to geological structure. His work in this field in New South Wales may be said to have laid the foundation for all later researches of similar character. In the sphere of economic geology he was equally a master, and his rare geological acumen is displayed in the monumental work on the Broken Hill lode. His studies of the distribution and evolution of floras in Australia and the Pacific Islands form a contribution of high and lasting merit.

Besides his work for our Society, Andrews interested himself widely in the administration of Australian Science. Among the organisations in which he was prominent were the Linnean Society of New South Wales, of which he was president in 1937; the Australian and New Zealand Association for the Advancement of Science, Honorary General Secretary 1922 to 1926 and President in 1930; the Australian National Research Council; and the Australian Institution of Mining and Metallurgy, President 1929. On a number of occasions he represented Australian Science at important international congresses.

Andrews received many honours besides those already mentioned, among which were honorary membership of the Washington Academy of Sciences and the Geological Society of America; honorary fellowship of the Royal Society of New Zealand; the Mueller Medal of the Australian and New Zealand Association for the Advancement of Science (1946); the Lyell Medal of the Geological Society of London (1931); and the David Syme Prize and Medal of the University of Melbourne. Through it all he remained a deeply serious and generous worker among his fellow scientists, among whom he was as much esteemed for his personal qualities as he was respected for his scientific attainments.

GEORGE FREDERICK BIRKS died May 4th, 1948. He was 82 years of age and had been a member of the Society since 1923. He was a member of the party which went to Paraguay under the leadership of William Lane to found a socialist colony. After he returned to Australia he entered upon a business career, later becoming a director of several undertakings and chairman of directors of Potter and Birks, Pty., Ltd., a firm of manufacturing chemists which was founded by him. He was much interested in the Rotary movement and was a World Vice-President of the Rotary International. He was also a devoted worker for crippled children, and the Activity School at the Royal Alexandra Hospital for Children is named after him.

ERNEST NORMAN MCKIE died May 19th, 1948. He was born at Guyra, New South Wales, in 1882, and spent most of his life around the New England district.

He at first intended to take up a business career and worked with the Commercial Banking Company of Sydney. Later he resigned to enter St. Andrew's College, Sydney University, from which he graduated as Bachelor of Arts in 1906. He completed the theological course in 1908 and took his first church appointment at Manilla, whence he moved to Bendemeer in 1909 and Guyra in 1912. He served as Moderator of the General Assembly of the Presbyterian Church in 1938.

Mr. McKie was an amateur botanist of distinction and had a detailed knowledge of the eucalypts and native grasses of the New England district. His knowledge and help were always available to research workers visiting the district. Beside his interest in botany he took an active part in movements to improve the standard of agriculture in his district, being the first secretary of the local branch of the New South Wales Agricultural Bureau, and for many years associated himself with the fostering of modern trends in agricultural work.

He was a member of the Australian Institute of Agricultural Science, the Linnean Society of New South Wales, to the *Journal* of which he contributed, and since 1932 of the Royal Society of New South Wales.

EDWARD MONTAGUE WELLISH, M.A., Emeritus Professor of Mathematics of University of Sydney, died after a short illness at his home in Roseville in July, 1948.

He entered the University in 1900 from Fort Street School after a brilliant pass at the Senior Examination in December, 1899, being equal with another student for the John West and Grahame Medals for general proficiency. He attended the evening classes, his guide in mathematics being the late Assistant Professor A. Newham. He graduated with first-class honours and the University Medal in Mathematics. He and Professor C. E. Weatherburn were awarded the University Medal for Mathematics for the M.A. degree in the year 1906.

In 1907 he was awarded the first Graduate Barker Scholarship and entered Emmanuel College, Cambridge, in October of that year. He commenced research in the Cavendish Laboratory under Sir J. J. Thomson. His research was on the theory of ionisation of gases, his chief papers during this period being "The Laws of Mobility and Diffusion of Ions formed in Gaseous Media", *Proceedings of the Cambridge Philosophical Society*, November, 1908; and "The Mobilities of the Ions Produced by Röntgen Rays in Gases and Vapours", *Transactions of the Royal Society of London*, January, 1909; and "The Passage of Electricity through Gaseous Mixtures", *Proceedings of the Royal Society of London*, June, 1909.

Emmanuel College awarded him a special scholarship and a little later the excellency of his work was emphasised by the award of the Clerk Maxwell Studentship. After graduating B.A. (Research) at Cambridge, Professor Wellish accepted the post of Assistant Professor at Yale University, U.S.A. In 1913 he published in the *Philosophical Magazine* "Experiments on Columnar Ionisation" and in the *American Journal of Science* he published two papers, "The Mobilities of Ions in Air" and "The Motion of Ions and Electrons through Gases".

He returned to Sydney in 1916 and was appointed to a lectureship in the Department of Mathematics and in 1926 he was given the status of Associate Professor of Applied Mathematics. His time for research in Physics was naturally restricted, his next papers appearing in 1924 and 1931, when he published "Photo-electrons and Negative Ions" in the *Proceedings of the Royal Society of London*.

During the nine years when Professors Carslaw and Room were absent from the Department of Mathematics, Professor Wellish was in charge. He retired in 1946, but to the regret of all his friends his health improved only slightly.

Professor Wellish was outstanding in his research, his lecture work and his administrative work. He rendered signal service on the Board of Secondary School Studies. As chief examiner in Mathematics for the Leaving Certificate Examination, he was always sympathetic to school teachers and their problems. His colleagues will always remember his consideration and kindness.

A CONTRIBUTION TO THE STRATIGRAPHY AND PHYSIOGRAPHY OF THE GLOUCESTER DISTRICT, N.S.W.

By P. B. ANDREWS, B.Sc.,
Teaching Fellow in Geology, University of Sydney.

With one text-figure.

Manuscript received, January 7, 1949. Read April 6, 1949.

I. INTRODUCTION.

In a recent paper (Osborne and Andrews, 1948) the geological structure of the northern end of the Stroud-Gloucester Trough was discussed. A full account of previous investigations and a geological map of the area were included in that work. The present paper deals with some aspects of the stratigraphy and physiography of the same area. The major contributions to these subjects have been those of Sussmilch (1921) and Voisey (1940), who have discussed the stratigraphy of part of the area in considerable detail. Carey and Browne (1938) and Voisey (1945) have also discussed the Carboniferous succession at Gloucester and have correlated it with those of other areas. The following notes are intended primarily to extend the work of these investigators, particularly to the areas immediately to the south and east which have an important bearing on the final elucidation of the geology of this interesting district.

II. STRATIGRAPHY.

(a) *Carboniferous.*

Sussmilch (1921) described a section across the Carboniferous strata on the west side of the Gloucester Trough in the neighbourhood of Barrington village and divided the sequence into the marine Burindi Series and the overlying terrestrial Kuttung Series. Carey and Browne (1938) further subdivided the Burindi Series into lower and upper sections, the Upper Burindi Series being the marine equivalent of the terrestrial Lower Kuttung Series of the Hunter River type area. Voisey (1940) described further sections from the same locality.

The recognition of a large fault separating the Devonian and Lower Burindi strata on the western side of the Trough (Osborne and Andrews, 1948) has confirmed the fact that the base of the Burindi Series is not exposed in these sections. The conglomerates outcropping on the Giro and Copeland Roads which are mentioned by Sussmilch and Voisey appear, however, to be close to the base of the series. A greater development of these conglomerates occurs

on the western side of the Barrington River on the "Manchester" Road, and here the following section was measured in descending order :

| | Feet |
|---|-------|
| Conglomerate and tuff | 220 |
| Tuff | 165 |
| Mudstones | 10 |
| Tuff and tuffaceous conglomerate | 35 |
| Tuffaceous conglomerate and mudstones | 120 |
| Tuff | 15 |
| Coarse conglomerate | 60 |
| Tuff | 30 |
| Tuffaceous conglomerate | 70 |
| Tuffs and mudstones | 85 |
| Tuff | 50 |
| Conglomerate | 15 |
| Tuffs and mudstones | 85 |
| Conglomerate | 25 |
| Tuffs and mudstones | 80 |
| Total | 1,065 |

The lowest beds in this sequence are separated by the Manchester Fault from Devonian rocks which outcrop on the flank of Mechanic's Mountain a short distance to the east. Figure 1 shows a columnar section of the Carboniferous strata in this neighbourhood and includes a revised estimate of the upper part of the Carboniferous sequence for the western side of the Stroud-Gloucester Trough.

The series which is shown in Figure 1, and which represents essentially the sections measured by previous workers, can be traced from the Bowman Road Fault, about $2\frac{1}{2}$ miles west of Gloucester, westwards to Barrington village, and thence southward to the Rawdon Vale Road in the vicinity of Cut Hill, where the beds appear to be cut off by an East-West fault.

Work in the area between the Rawdon Vale Road and Spring Creek on the western side of the Trough, and also on the eastern side between the Gloucester-Taree road and Ward's River, has shown, however, that this type section is not developed in any other part of the Gloucester-Stratford district, and none of the datum beds which have been referred to have been located elsewhere in the area.

Owing to the extensive faulting which has taken place, it was found impossible to measure a complete section of the Carboniferous Series on the eastern side of the Trough. Strata of Lower Burindi age outcrop in the country immediately to the south of the Gloucester-Krambach road from a point near the junction of the Mograni Creek road, east at least as far as Gangat, being cut off by faults from Devonian strata to the north and Upper Kuttung and Upper Burindi rocks to the south. These beds consist of mudstones and tuffs dipping steeply to the north. In Brushy Cutting near Gangat a thick series of greenish-grey friable mudstones with subordinate thin bands of tuff is exposed along the road. These beds closely resemble those of the Lower Burindi Series on the west side of the Trough. No fossils have been found in them.

An approximate section of the Upper Burindi and Upper Kuttung rocks on the eastern side of the Trough was measured from Mograni Creek School in a westerly direction. This revealed a total thickness of about 7,400 feet for the Upper Burindi Series, consisting essentially of felspathic and pebbly tuffs and mudstones. These beds are very similar to those of the Upper Burindi Series

on the western side of the Trough, but no fossils were found in them. Over much of this area the beds are dipping vertically, and it is probable that some strike faulting has occurred, thus accounting for the very great thickness measured for the series.

About halfway up in this section is a flow, about 20 feet thick, of green dacitic pitchstone which was traced along its strike for about $1\frac{1}{4}$ miles but lenses out. Under the microscope the groundmass of this rock is seen to be partly glassy, but is crowded with microlites. A few corroded phenocrysts of quartz are scattered through the rock, and clusters of oligoclase phenocrysts are also present. This may possibly be correlated with a very similar flow which outcrops for a short distance on the ridge to the south of the Rawdon Vale road, where it crosses Out Hill, where it immediately underlies the topmost flow of quartz-keratophyre in the Upper Burindi sequence.

The top of the first main ridge in the Mograni section is composed of a coarse tuffaceous conglomerate which was considered to be the basal bed of the Upper Kuttung Series, the overlying beds consisting almost entirely of pebbly tuffs and conglomerates in which some obscure plant remains were found. Farther to the south Upper Burindi strata outcrop along the Waukivory Road, and here consist of mudstones and light-coloured coarse felspathic tuffs. Marine fossils were found in Portion 211, A. A. Coy's Grant, close to the road, in a locality mentioned by Voisey (1940). These were not sufficiently well preserved for identification, but included pelecypods and a small gastropod. On the ridge between this point and Phillip's Creek a bed of coarse tuff was found which contains crinoid stems, but most of the considerable thickness of pebbly tuffs and mudstones are apparently unfossiliferous. The presence of the East Stratford Fault, which separates these beds from the Upper Kuttung Series, prevents the determination of the exact position in the sequence of the fossiliferous horizons.

The rugged country at the head of Dog Trap Creek and Ward's River consists of a great thickness of apparently unfossiliferous tuffs and tuffaceous conglomerates with subordinate mudstones. The ridge on which is situated Craven Trigonometrical Station is formed of one of the beds of coarse tuffaceous conglomerate. These sedi-

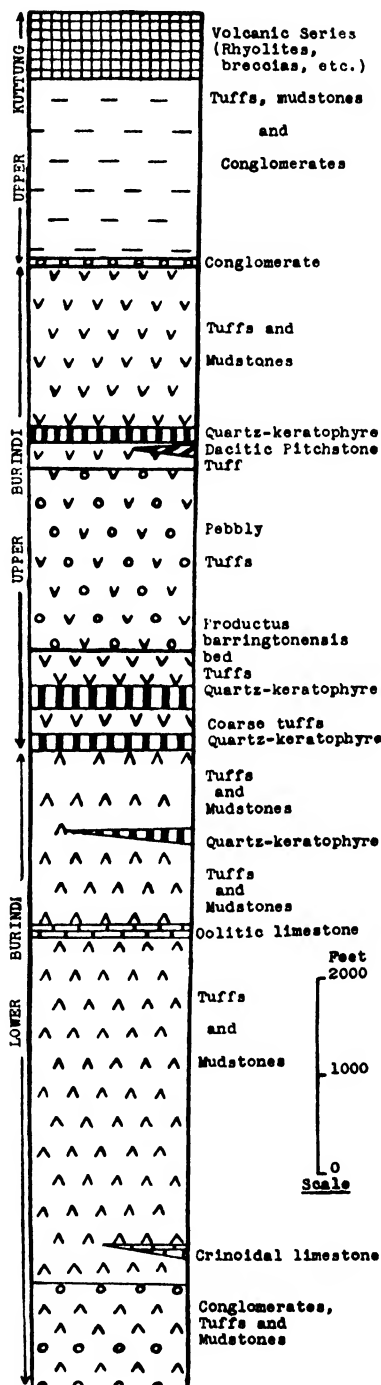


Fig.1. Generalised Section of Carboniferous Strata on western side of Stroud-Gloucester Trough.

ments are again very similar to those of the Upper Burindi Series on the western side and are provisionally correlated with them. In this neighbourhood the strata dip to the east at angles of about 70 degrees and are cut off on the west by the East Stratford Fault.

The steep ridges on the western side of the Stroud-Gloucester Trough, south of the Rawdon Vale road, also consist almost entirely of pebbly tuffs. However, a flow of rhyolite forms the highest part of the ridge between Cut Hill Creek and the upper Avon River. South of the Avon River the crest of the Faulkland Range is formed of another thin flow of acid lava, in this case a light grey, wholly glassy rock with numerous veinlets of quartz. Here, however, the associated sediments, which include dark-coloured cherts and a few thin beds of carbonaceous shale, appear to belong to the Upper Kuttung Series. Pebbly tuffs and mudstones which outcrop on the western flank of the Faulklands Range are believed to be of Upper Burindi age, but no detailed work was carried out in this locality.

Carey and Browne (1938) suggested that the type section of the Upper Burindi Series on the western side of the Gloucester Buckets Range was a predominantly terrestrial sequence with thin marine intercalations. Voisey (1945) considers that the whole of the Upper Burindi Series is marine. A careful study of these beds has shown that fragments of marine fossils are widely distributed through the series, but it is possible that there are some terrestrial sediments interbedded in an essentially marine sequence. It must be emphasized that the whole facies is indicative of shore-line conditions.

The almost complete absence of marine fossils from the corresponding beds on the eastern side of the Trough may indicate that this particular area was one of predominantly terrestrial deposition, the same types of tuffs and pebbly beds being present as in the marine series on the western side. It is also significant that no marine fossils have been found in similar beds on the western side farther south than the Rawdon Vale road.

Thus it is probable that much of the strata indicated on the previously published map (Osborne and Andrews, 1948) as belonging to the Upper Burindi Series is, in fact, of terrestrial origin. As the distinction is purely one of facies and not of age it has been considered advantageous to classify all these rocks under a single head.

The most notable feature of the Upper Kuttung Series in the Gloucester-Stratford district is the great development of volcanic rocks. These have been discussed by Sussmilch (1921) under the name of the "Gloucester Rhyolites", but Voisey (1945) has pointed out that the greater part of the volcanic series consists of fragmental material. This is particularly the case on the eastern side of the Stroud-Gloucester Trough where these strata attain their greatest development. The total thickness of the volcanic series in the neighbourhood of Mograni Mountain is about 3,000 feet. No attempt has been made to map individual flows, of which there are a large number, but many different varieties have been collected. A great deal of brecciated material is present, the fragments consisting largely of banded rhyolites and tuffs of several kinds. Many of the lavas exhibit large vughs and veins filled with chalcedony, and it is interesting to note that this is also the case at Pokolbin, where lavas occur which are almost identical chemically with some of those of the Gloucester Buckets Range. The lavas range in composition from rhyolites to andesites, blue dacites showing strong flow structure being particularly well developed in the vicinity of Oak Creek Falls.

The Upper Kuttung Series to the west of Stratford and Craven consists almost entirely of tuffs and tuffaceous conglomerates, and the typical volcanic sequence is not developed, although it still appears in the ranges on the east

side of the valley. At the head of the Upper Avon road, pink and purplish volcanic breccias outcrop, but these are of an entirely different type from the brecciated lavas of Mograni Mountain.

(b) *Permian.*

Rocks of Permian age occupy the central part of the Stroud-Gloucester Trough and consist of conglomerates, grits, sandstones, shales and coal seams. These beds have been assumed to belong to the Upper Coal Measures (Sussmilch, 1921 ; Voisey, 1940) but no direct correlation can be made as they are isolated from the main coal basin of the Hunter River Valley and a correlation based purely on lithological similarities cannot therefore be accepted.

Owing to the presence of much minor folding and variations in dip, and to the paucity of good outcrops, the thickness of the Coal Measures cannot be accurately measured, but in the neighbourhood of Gloucester there is a total thickness of at least 1,900 feet. No clearly defined junction between these beds and the underlying Upper Kuttung Series has yet been found, owing to the characteristic talus slopes which everywhere mark the boundary of the volcanic series, but in a track cutting close to the Barrington River near Kiaora Crossing, and in the railway cutting immediately north of the bridge over the Avon River, the two series appear to be separated by an erosional disconformity, the Permian rocks occupying hollows in the surface of the Upper Kuttung lavas. The basal bed of the Permian sequence wherever studied is a coarse conglomerate containing pebbles of rhyolite and tuff which gives further evidence of a probable erosional break between the two series.

The best exposures of the Coal Measures are to be seen in the railway cuttings between Spring Creek and Craven, in the southern part of the area under discussion. A large number of outcrops of coal seams appear in these cuttings, but most of the seams are very thin. These beds show many minor folds and faults (Osborne and Andrews, 1948). In the bed of Coal Creek about one-quarter mile south of Craven Railway Station a section was measured totalling 146 feet of sediments, of which 24 feet is coal, but this is distributed between thirteen distinct seams.

To the east of Craven, along the Glen road and south at least as far as Stoney Creek, is a faulted outlier of Coal Measures consisting essentially of sandstone and conglomerate. A 14-foot seam of coal is exposed in the bed of Stoney Creek a short distance above its confluence with Ward's River.

III. PHYSIOGRAPHY.

Sussmilch (1921) briefly discussed the major physiographic features of the Gloucester district and mentioned the contrast between the relatively flat and low-lying valley of the Gloucester, Avon and Ward's Rivers, excavated in soft Permian strata, and the steep country on either side occupied by Carboniferous rocks.

Extensive alluviation of the lower reaches of the Gloucester and Avon Rivers at the northern end of the valley has taken place, and this is probably partly due to the blocking of the Gloucester River immediately above its junction with the Barrington River by a hard bar of Carboniferous lavas which is an extension of the Mograni Range. This would have formed a local base-level for the river. This is confirmed by the presence of a river terrace which is revealed in a road cutting where the river passes on the north side of the town of Gloucester and which is about 40 feet above the present river level.

In the main valley, the divide between the Avon River system flowing northward and the Ward's River system flowing to the south is very low and

irregular. Ward's River flows out of the ranges on the eastern side in a narrow valley at an average elevation about 100 feet lower than the land immediately to the north, and its tributaries, cutting back in this direction, threaten to capture the headwaters of Swamp Creek which now flows over an almost level plain before joining the Avon River. In a similar way Spring Creek, which flows into Ward's River from the west, threatens to capture the heads of some of the small creeks which flow northward to the Avon River on the western side of the North Coast Railway. If these changes were to take place the whole drainage pattern of the Avon River would be reversed.

Sussmilch noted that the main stream channels appear to antedate the present topography, and it may be noted that this also applies to many of the smaller streams, which have cut across hard and weak structures alike. On the eastern side of the main valley Ward's River, Waukivory Creek, Dog Trap Creek and Mograni Creek all rise in the country to the east of the Mograni Range and have cut steep gorges through it as they flow westward, cutting at right angles across the general trend of the country to do so. Waukivory Creek flows in a relatively mature valley on the eastern side before plunging into a narrow gorge through the range, which rises to a height of over 1,000 feet on either side.

In the same way the Gloucester River and Gap Creek have cut through the Gloucester Buckets Range on the western side. The case of Gap Creek is particularly noteworthy, as it rises in low hills within a mile of the Barrington River, but flows eastward by way of a deep and narrow gorge through the Gloucester Buckets into the Gloucester River.

The course of the Barrington River is of great interest. Between Berrico and Faulklands are a series of entrenched meanders, but at the latter locality the river turns sharply and flows northward, approximately parallel to the strike of the Carboniferous strata. Where the strike of these rocks swings round to the east in the vicinity of Barrington village the river continues northward for another mile and then turns sharply to the east. Farther downstream the river flows approximately parallel to the strike of the Devonian strata on the northern bank, but here its course is determined primarily by the presence of the Barrington River Fault. The reasons for the two abrupt changes of course are difficult to visualize, but that at Faulklands may have been caused by piracy of the head of the old river by a young stream cutting back along the strike from the north, the old river having previously flowed to the east, as is still the case with the Gloucester River.

IV. CONCLUSION.

The above notes are intended primarily to extend the work of previous investigators and to present some aspects of the stratigraphy and physiography of the Gloucester-Stratford district which have not previously been discussed. It is emphasized that the important Carboniferous sequence of the western side of the Stroud-Gloucester Trough, which has been the subject of much discussion is developed only within a comparatively limited area, and in particular is not found on the eastern side of the Trough in the neighbourhood of Gloucester.

V. ACKNOWLEDGEMENTS.

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THE EFFECT OF DIFFUSIONAL PROCESSES ON THE RATE OF CORROSION.

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LIMITATIONS OF CORROSION TESTS.

Reviews of corrosion test procedure by White (1934), McKay and La Que (1937), La Que and Knapp (1945) and by others have stressed the necessity for a very close standardization of conditions. If measurements of the rate of loss of mass from a metal test piece in a given corrodant liquid are to be any guide to the behaviour of metal members under large-scale conditions, very close attention must be paid to a number of details, such as the depth of immersion, the methods of suspension or support and the conditions of aeration and circulation of the fluid ; as well as to such more obvious factors as the temperature and pH of the corrodant liquid and the presence or absence of other metals forming electro-chemical couples with the test specimen. White, indeed, has emphasized the difficulty in getting reproducible results even with different specimens of the same dimensions, and La Que and Knapp have stressed the necessity for a detailed evaluation of the proposed conditions of application in order that these may be duplicated as closely as possible in the laboratory tests.

The overall reaction of a metal dissolving in an electrolyte to give either a soluble or insoluble ionic product has long been recognized as a complicated one. Many successive physical and chemical operations are involved. Much attention has recently been given to some of these operations, especially those of a more chemical nature, such as interphase ionic transfer, anodic and cathodic polarization, and the effect thereon of inhibitors and accelerators. On the other hand the effect of the transport processes which bring the active depolarizing agent up to the seat of attack and remove therefrom the products of reaction has not received such close attention. It is clear, for example, that in the corrosion of copper by acetic acid in which the reaction is maintained by cathodic depolarization produced by dissolved oxygen, the maintenance of the chemical attack is dependent on the continuity of the supply of oxygen to the cathodic areas ; and it is conceivable that, under certain conditions, the rate of diffusion of oxygen might become a rate determining factor.

The conception of a set of physical transport phenomena entering into the final determination of the rate of chemical attack by a corrodant liquid is one which has been paralleled in recent years in other fields of applied chemistry. Thus Damköhler (1936), Edgeworth Johnstone (1939), Laupichler (1938), Hurt (1945) and Bosworth (1947) have all discussed the effect of such factors as the flow of heat and flow of reactants and resultants on the course of chemical reactions in small and large scale reactors. Further, Agar and Hoar (1948) have discussed the effect of a change of scale on an electrochemical system and have concluded that the rate controlling step for a large scale system is not necessarily the same as for a small scale system under otherwise identical chemical and physical conditions.

VARIABLES OF THE TRANSPORT PROCESS.

It appears desirable, therefore, to examine the process of corrosion with a view to enumerating and, if possible, devising methods of measuring the factors which are concerned in the transport of matter to and from the corroding surface. In this object there is one obvious mode of attack. Recently a number of authors (Sutton, 1934 ; Powell and Griffiths, 1939 ; Pasquill, 1943 ; and Boelter, Gordon and Griffin, 1946) have traced a degree of parallelism between heat loss and loss of matter by evaporation from geometrically similar bodies. Since it is not unreasonable to expect that matter loss from corroding bodies might also behave similarly, and further since the laws of conduction and convection of heat are particularly well known, the first object of this paper and of the two succeeding papers will be an attempt to trace a degree of parallelism between heat loss and matter loss by corrosion from geometrically similar bodies. This paper will be specifically concerned with transport under stagnant fluid conditions, analogous to the transport of heat in a fluid by thermal conductivity alone.

The corrosion rate q , in mass flow per unit area per unit time, and the corrosion cell e.m.f. E are, clearly, two of the properties with which we will be concerned. The quantity E is the driving force which produces a flow of matter q . While much has been discovered from purely electrochemical measurements concerning the mechanism whereby E produces the matter flow q , we are not here immediately concerned with this subject. We are, however, concerned with the property which might be defined as the overall chemical resistance (or impedance) of the system—that is to say the factor which determines the magnitude of the driving force required to produce a given flow rate. Since various successive reactions are involved in the corrosion process, this overall resistance can presumably be split into a number of series (or parallel) components, one corresponding to each step in the corrosion process ; in much the same way as the flow of heat in a multi-component system can be represented by a number of series (or parallel) thermal resistances. Among the factors contributing components to the overall chemical resistance are the transport processes leading to the removal of the anodic and cathodic products of corrosion from the immediate vicinity of the interface under attack. Removal may be effected by diffusion, turbulent diffusion, or by the convection currents set up either as a result of density changes produced by the solution of heavy metal ions, or from temperature changes. Since the mechanism of removal of the products of reaction controls the degree of polarization, it also controls the magnitude of the electric current across the metal-electrolyte interface and thus the rate of corrosion. The transport processes involved in the removal of matter from the vicinity of the interface bear a formal similarity to those exhibited by the heat loss from a hot body immersed in a fluid. Heat may be carried from such a body by molecular conduction, turbulent conduction, by forced convection if the fluid is stirred, or by natural convection.

Examples of corrosion in which an insoluble phase resulting from chemical reaction consequent to corrosion builds up a barrier to the diffusion process, or those in which the corrosion reaction is maintained by the presence of a bimetallic system providing a permanent cell e.m.f. obviously involve a transport mechanism which is more complicated than that involved in the flow of heat. However, when uniform, or general corrosion alone occurs, it would appear that the transport processes have features in common, and it is this suggested similarity which will be discussed below.

EXPERIMENTAL.

The subjects of experimentation were selected so as to avoid the more complicated types of corrosive attack. The subjects consisted of copper,

certain copper alloys and steels in acetic acid-acetic anhydride mixtures. Commercial acetic acid has a high electrical resistivity of the order 1.5×10^{-6} ohm-cms., and accordingly bimetallic corrosion is not serious. The acetates are soluble, and thus complications due to the formation of barriers are avoided. Further, experience has shown that these systems do not show the phenomenon of dezincification in which one component of an alloy selectively dissolves. The only type of corrosion is a general attack all over the surface exposed to the acid. Accordingly these systems are particularly suitable for the examination of the influence of convection on the process of corrosion.

The equipment used consisted of a cylindrical body C of the metal under test, 3 cms. in diameter and 1.8 cms. long. One flat face of this body contained a cylindrical hole 1.0 cm. in diameter and 0.8 cm. deep coaxial with the body as a whole. Into this hole there fitted snugly a second cylinder, B, of the same metal, the two top faces being coplanar. These two faces were polished together. Cylinder B was removed and weighed and then placed back in position. The air was pressed out through a hole at the back of C, and this hole was finally closed by means of a screw also of the same metal. A thin film of an acid-proof grease used for lubrication prevented the corrodant from coming into contact with any portion of B other than the front face. This equipment thus permitted a study of the attack on a definite area of a single metal face surrounded on all sides by a surface of the same metal, which thus acted as a guard ring and, by eliminating irregularities in the field of the corrodant at the edges, reduced the geometrical pattern of the flow of matter to and from the face under attack to one in a single dimension.

After subjection to the corrosive conditions for a measured time, cylinder B was removed, the acid-proof grease was dissolved in a volatile solvent and the cylinder dried and weighed.

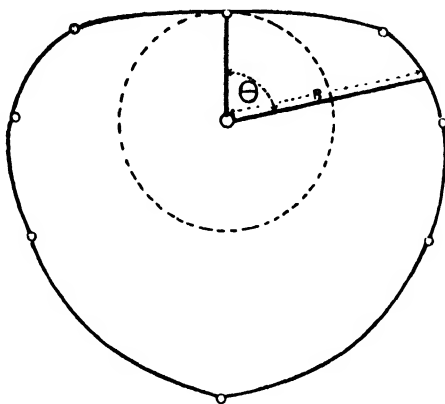


Fig. 1.

THE EFFECT OF ORIENTATION.

The equipment as described above was first used in a study of the effect of orientation on the rate of corrosion. An iron (mild steel) surface was immersed 4 cms. in a 60/40 acetic acid-acetic anhydride mixture and the rate of corrosion measured at different orientations as the face was turned in a vertical plane through 2π . The results are shown in the form of a vector diagram in Figure 1. In this diagram the r co-ordinate measures the rate of corrosion and the θ co-ordinate the azimuth.

It will be seen from the figure that the rate of loss of matter is a minimum when the corroding surface is facing upwards and a maximum when facing downwards. Evans and Mears (1934) have already remarked on the flow of heavy metal salt solution under gravity away from all surfaces except those facing vertically upwards. This flow constitutes a convection current opposite in direction, but essentially similar in nature, to the convection currents surrounding a hot body in a fluid. Thus it is seen from Figure 1 that the corrosion rate is a maximum when the convection current is most intense and a minimum when there is no convection and when the loss of matter takes place entirely by a "conductive" mechanism.

In taking measurements of the corrosion rate with all transport processes restricted to those of the "conductive" type, it is of importance to be able to estimate the error involved in any slight departure of the surface from the horizontal position—say by an angle θ . Since the top of Figure 1 is flat, it follows that the error is of the order $q/\cos \theta$ or $q(1 + \theta^2)$, where q is the measured rate. Errors of magnitude sensible in comparison with the random errors usual even in the best corrosion measurements are thus not incurred unless θ is greater than 0.2 radian or 12° , which quantity is thus a measure of the tolerance allowed on the orientation.

EFFECT OF VARYING THE DEPTH OF IMMERSION.

The property of thermal conductivity plays a large part in all successful attempts at the co-ordination of experimental determinations on the rate of conductive and convective transfer of heat. If a similar co-ordination of the effects of convection on the corrosive transfer of matter is to be attempted, it is

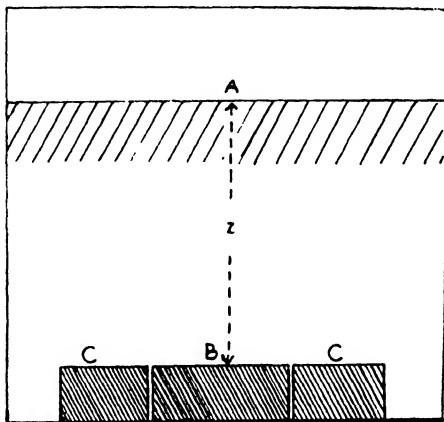


Fig. 2.

important to find that property concerned with the transport processes involved in corrosion which plays the same part as thermal conductivity does to heat flow in fluids. Such a property could be measured by an adaption of the guard-ring method of measuring thermal conductivity. If we set up the equipment, described in the section above, horizontally at a distance z below a free surface, we will effectively be concerned with one-dimensional diffusion through a distance z , the depolarizing agent (atmospheric oxygen) having to travel that distance through a stagnant layer of the corroding liquid.

In Figure 2, let A represent the free surface of the corroding liquid and B and C respectively the surface under attack and the guard-ring both at a distance z from the free surface and parallel to it. We are concerned with a flow of matter

from B to the liquid ; the flow, on account of the influence of the guard-ring, being normal to the surface. This flow, the magnitude q of which may be measured by weighing the central cylinder before and after a measured time interval, is stoichiometrically connected with all chemical steps in the corrosion reaction. One of these steps is the "conductive" flow of the depolarizing agent through a distance z . The magnitude of q therefore might be expected to vary with z in the same way as the flow of heat from a geometrically similar hot plate separated from another plate, at a temperature difference θ from the former, by a convectionless thermal conductor of conductivity k_θ . In such a thermal system the heat flow q_θ per unit area per unit time is related to θ by an equation :

$$k_\theta = \frac{q_\theta z}{\theta}.$$

If dq_θ is the heat flow change associated with a change dz in the thickness of the thermal conductor, we have

$$k_\theta = \frac{1}{\theta} \frac{dz}{d(1/q_\theta)} \dots\dots\dots (1)$$

In the mass flow system involved in the corrosion process we may readily measure the change in the rate of corrosion (dq), in units of mass crossing unit area in unit time, produced by a change dz in the length of the path through which the depolarizing agent is conducted. In this system now we may define a corresponding conductivity term k_c by means of an expression analogous to equation (1), viz.

$$k_c = \frac{1}{E} \frac{dz}{d(1/q)}, \dots\dots\dots (2)$$

where by E is to be understood the overall driving force for the corrosion reaction, or the corrosion cell e.m.f.

If for a given system k_c is a constant, or if in other words the system follows a law analogous to Fourier's law, then we expect to get a straight line when the depth z is plotted against the reciprocal of the rate of corrosion ($1/q$). Experimental data obtained on the guard-ring equipment are represented in Figures 3 and 4, where $1000/q$ is plotted against z for the different systems studied. The experiments were conducted in a thermostat at two different temperatures, namely 20° C. and 70° C. The $1/q$ versus z lines are straight, but do not pass through the origin. Each system may thus be described by two constants; the intercepts $1/q_0$ on the $1/q$ axes which incidentally are always positive, and

the slopes $\left(\frac{dz}{d(1/q)} \right)$, which we shall denote hereunder by the symbol j . We

see, therefore, that the process of transport of matter involved in a corrosion reaction taking place under "conductive" conditions involves two properties of the system, j and q_0 . The significance of these properties will be discussed below, but first it is desirable to consider the units in which these quantities are to be measured and the magnitude of these properties for typical systems.

UNITS.

Many problems connected with the transport of matter and of heat which are too complicated for a complete mathematical treatment have been successfully treated by the use of dimensionless quantities. In order to combine the quantities connected with the transport phenomena concerned with corrosion, it is first necessary to use a consistent set of units throughout. The various phenomena involved can be reduced to four fundamental dimensions. Now q the rate of corrosion is, in the technical literature, commonly measured in units

of milligrammes decimetres⁻² days⁻¹, while E , the corrosion cell e.m.f., is commonly measured in volts. We shall accordingly take for our four fundamental units the quantities, decimetres, milligrammes, days and volts. Thus the quantity j above is to be measured in milligrammes decimetres⁻¹ days⁻¹, while k_c is to be measured in milligrammes decimetres⁻¹ days⁻¹ volts⁻¹.

The units in which the other properties of importance are to be measured will be given later. For convenience this system of units will be referred to as the d.m.d.v. system.

RESULTS.

The experimental results calculated from the lines shown in Figures 3 and 4 are tabulated in Table 1. For each system and temperature studied the two properties j and q_0 are recorded, each of course, in d.m.d.v. units.

TABLE 1.

| Metal. | Corrodant. | Temperature. | Slope j Milligrammes dm ⁻¹ , day ⁻¹ . | Reciprocal Intercept q_0 Milligrammes dm ⁻² , day ⁻¹ . |
|---------------------|------------------------------------|--------------|---|---|
| Copper. | Acetic anhydride | 20° C. | 9.6 | 51 |
| „ | 60/40 acetic acid/acetic anhydride | „ | 10.5 | 125 |
| „ | Glacial acetic acid | „ | 13.8 | 150 |
| „ | 50% aqueous acetic acid | „ | 6.0 | 97 |
| „ | 50/50 acetic acid/benzene | „ | 195 | 405 |
| „ | 60/40 acetic acid/acetic anhydride | 70° C. | 190 | 2000 |
| „ | Glacial acetic acid | „ | 710 | 2000 |
| Brass. | Acetic anhydride | 20° C. | 1.6 | 71 |
| „ | 60/40 acetic acid/acetic anhydride | „ | 6.2 | 66 |
| „ | 50% aqueous acetic acid. | „ | 3.3 | 70 |
| Phosphor bronze. | 60/40 acetic acid/acetic anhydride | 20° C. | 18.2 | 135 |
| „ | Glacial acetic acid | „ | 20.0 | 130 |
| „ | 50% aqueous acetic acid | „ | 16.0 | 100 |
| „ | Glacial acetic acid | 70° C. | 660 | 1050 |
| Mild steel. | 60/40 acetic acid/acetic anhydride | 20° C. | 52.0 | 1000 |
| „ | Glacial acetic acid | „ | 62.0 | 950 |

DISCUSSION.

The lines represented on Figures 3 and 4 relating the variation of the rate of corrosion with the depth can be put in the form

$$\frac{1}{q} = \frac{1}{q_0} + \frac{z}{j} \dots \dots \dots (3)$$

A similar expression would have been given for the heat loss across a thermal conductor of various thickness from a hot body, which however is not bare but thermally lagged so that the rate of heat loss can never exceed a certain figure.

The property j is related to the correction conductivity k_c by the expression

$$j = Ek_c \dots \dots \dots (4)$$

and is more convenient than k_c because the quantity E is not directly concerned in corrosion measurements. The quantity j is a measure of the conductivity of the corrodant for the depolarizing agent and is thus a measure of a sensitivity of

the reaction concerned to control through limiting the supply of depolarizing agent. A reaction giving a small j such as brass in acetic anhydride is strongly dependant on the supply of atmospheric oxygen.

The quantity q_0 is a measure of the rate of corrosion when the depolarizing agent is made instantly available at the surface and is thus a quantity of more direct chemical significance than measures of q under any standard conditions of

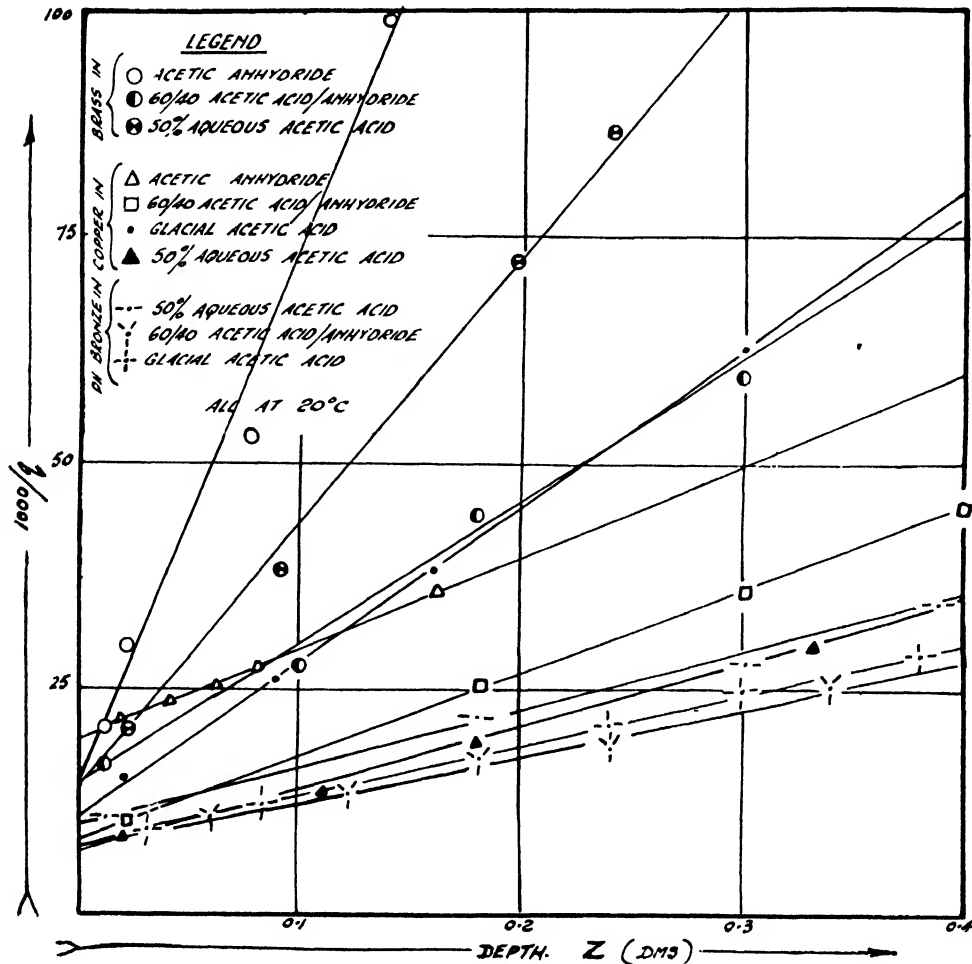


Fig. 3.

immersion or aeration. The ratio E/q_0 is a measure of the resistive force opposing the corrosion process when the effect of all physical factors limiting the supply of the depolarizing agent to the surface have been eliminated. If we denote this resistance by r , viz.

$$r = E/q_0 \dots\dots\dots (5)$$

We then have, for the net driving force available for maintaining the transport of depolarizing agent to the surface under attack when the specimen is corroding at a rate q ,

$$E - qr \text{ or } E(1 - q/q_0) \text{ volts.}$$

This is the factor with which we will be concerned in treating the more complicated phenomena concerned with transport processes involving forced and natural convection.

SUMMARY.

The influence of the processes involving the transport of matter on the rate of corrosion has been studied by means of a circular disc protected by a guard-ring. This device reduced the geometrical nature of the flow of matter to one in a single dimension. The variation of the corrosion rate of such a surface was

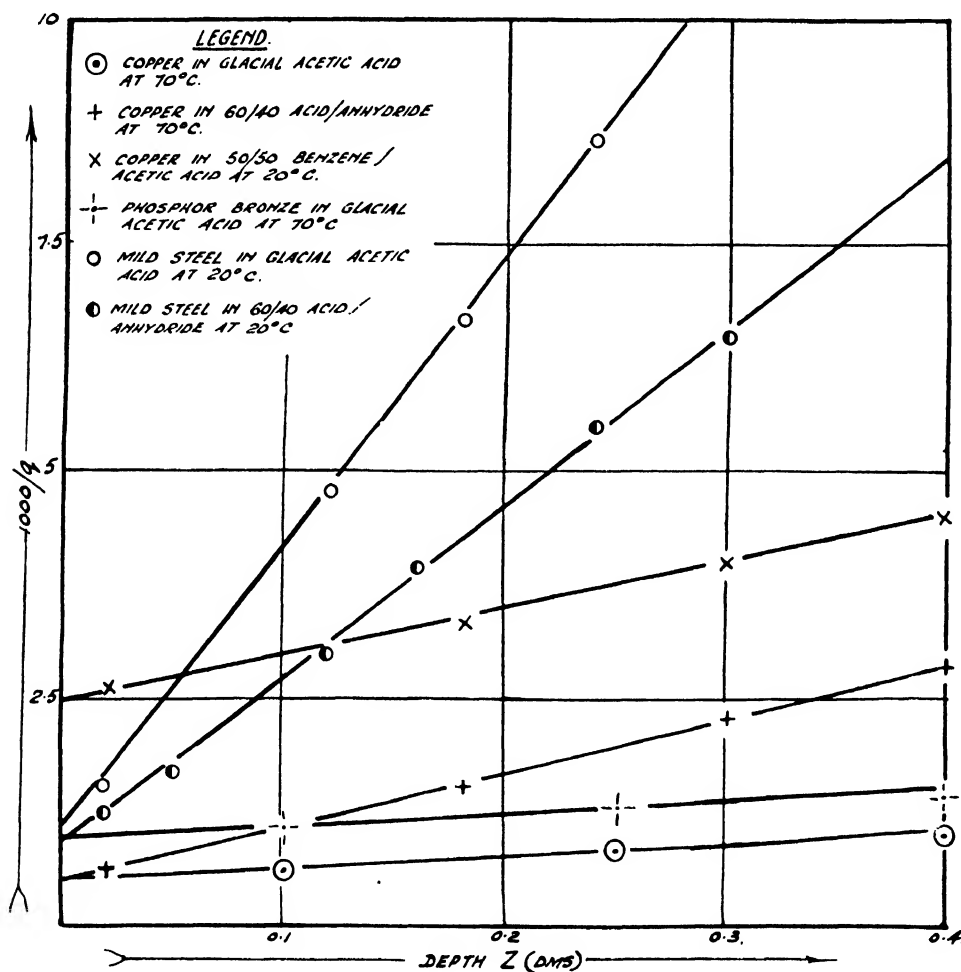


Fig. 4.

studied as a function of the orientation of the surface and shown to be a minimum when it faced upwards. It was concluded that convective transfer was absent under these conditions. The corrosion rate, from a horizontal surface facing upwards and protected by an electro-chemical guard-ring, was then studied as a function of the depth of immersion.

The systems studied included copper, copper alloys and steel in acetic acid, acetic anhydride mixtures. Experimental results plotted in the form : reciprocal

of the corrosion rate ($1/q$) versus the depth (z) of immersion give straight lines with positive intercepts on the $1/q$ axis. These intercepts have been interpreted as a measure of the rate of corrosion under such conditions that the depolarizing agent (atmospheric oxygen) is made freely available at the surface. The slopes have been interpreted as a measure of the "conductivity" of the corrodant for the depolarizing agent, a factor which, it is suggested, would be of primary importance in the interpretation of the effect of convection of the rate of corrosion.

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THE INFLUENCE OF FORCED CONVECTION ON THE PROCESS OF CORROSION.

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INTRODUCTION.

That the phenomena occurring at the interface between a fluid electrolyte and an electrode, usually solid, can be influenced by the mechanism available for the transport of ions in the fluid has been recognized since the days of Nernst (1904). Nernst introduced the concept of a *diffusion layer* as that of a quiescent fluid zone of definite thickness across which matter may be transferred only by molecular conduction and in which no convection currents occur. The bulk of the fluid outside the diffusion layer is assumed to be so well stirred up by convection as to be effectively at uniform concentration. It then follows that the rate of transfer to the interface is governed by the product of the concentration difference across the diffusion layer, the diffusivity in the layer and the reciprocal of the thickness of the layer. Since the diffusivity is a specific property of the system concerned the diffusion layer thickness is the property which determines the influence of concentration difference on the rate of transfer.

The Nernst concept of a *diffusion layer* has been extended by Levich (1942, 1944, 1947) to that of a *diffusion boundary layer* defined by analogy with the boundary layers of hydrodynamics and of thermal convection. Agar (1947) has used this concept of a diffusion boundary layer treated as a Nernst diffusion layer in order to estimate the influence of the current density on overvoltage, and has applied his figures specifically to the deposition of iodine. His method is based on an assumed analogy between matter flow and heat flow both under conditions of natural convection and the final figures he obtains supports his initial assumptions. He makes no use of the analogy other than that of determining boundary layer thicknesses and associated properties.

In a series of measurements on the rate of transfer of metal ions from solid metal to liquid electrolyte—or measurements of the rate of corrosion of certain metals by acids—under such conditions that all convection currents could reasonably be presumed to have been eliminated, the author (Bosworth, 1949) was led to infer a possible analogy between corrosive matter loss and convective heat loss from a lagged hot body geometrically similar to the one undergoing corrosion. It is clear that if this analogy could further be developed it would yield information on other properties concerned in the transport of matter as well as the diffusion boundary layer thickness. This, and the succeeding paper, will describe attempts to study the behaviour of corroding bodies under regulated conditions of forced and natural convection by the same method as that which has proved so successful in heat transfer problems; namely by the use of dimensionless quantities analogous to the Nusselt, Prandtl, Peclet and Grashof numbers.

THE TABLE OF ANALOGOUS PROPERTIES.

Table 1 below gives, on the left-hand side, a list of the properties and their units used in the treatment of forced and natural convection from a cylindrical

TABLE 1.

| Thermal Properties. | | | Properties Connected with Corrosion. | | |
|---|--|--|--|-------------------------------------|---|
| Property. | Symbol. | Unit. | Property. | Symbol. | Unit. |
| Heat Flux | q | cal. cm. ⁻² sec. ⁻¹ . | Corrosion rate | q | mgrms. dm. ⁻² day ⁻¹ . |
| Temperature difference .. | θ | ° C. | Limiting corrosion rate .. | q_0 | mgrms. dm. ⁻² day ⁻¹ . |
| Transmittance | h | cal. cm. ⁻² sec. ⁻¹ ° C. ⁻¹ | Effective cell e.m.f.... | $E(1 - q/q_0)$ | volts. |
| Thermal conductivity .. | k | cal. cm. ⁻¹ ° C. ⁻¹ sec. ⁻¹ | — | $\frac{q}{E(1 - q/q_0)}$ | mgrms. dm. ⁻² day ⁻¹ volt ⁻¹ . |
| Diameter of hot body .. | d | cms. | — | $\frac{E(1 - q/q_0)}{j/E}$ | mgrms. dm. ⁻¹ day ⁻¹ volt ⁻¹ . |
| Length of hot body .. | l | cms. | Diameter of corroding body | d | dms. |
| Mass rate of flow .. | γ | grms. sec. ⁻¹ . | Length of corroding body | l | dms. |
| Viscosity | η | poises. | Mass rate of flow .. | γ | mgrms. day ⁻¹ . |
| Acceleration due to gravity .. | $g(981)$ | cms. sec. ⁻² . | Viscosity | η | mgrms. dm. ⁻¹ day ⁻¹ . |
| Heat capacity (Const. p) .. | c_p | cal. gm. ⁻¹ ° C. ⁻¹ . | Acceleration due to gravity | $g(7.32.10^{11})$ | dm. day ⁻² . |
| Density | ρ | grms. cms. ⁻³ . | — | — | — |
| Quantity of heat per unit volume. | $c_p \rho \theta$ | cal. cms. ⁻³ . | Density | ρ | mgrms. litre ⁻¹ . |
| Volumetric heat capacity .. | $c_p \rho$ | cal. cm. ⁻³ ° C. ⁻¹ . | Quantity of corrodant per unit volume. | $\frac{\rho}{C}$ | mgrms. litre ⁻¹ . |
| Coefficient of volumetric expansion | $\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial \theta}$ | ° C. ⁻¹ . | Quantity of corrodant per unit volume required to change E by unity. | $K = \frac{\partial C}{\partial E}$ | mgrms. litre ⁻¹ volt ⁻¹ . |
| Thermometric conductivity | $\alpha = \frac{k}{c_p \rho}$ | cms. ² sec. ⁻¹ . | Diffusivity of corrodant .. | $D_c = \frac{j}{EK}$ | dm. ² day ⁻¹ . |

body. On the right-hand side the corresponding properties associated with the flow of the depolarizing agent to a corroding body are given with their units and suggested symbols. The units have been selected in such a way as to be consistent with the usual technical measurements of q (the rate of corrosion) in milligrammes decimetres⁻² days⁻¹ or 8.64×10^8 C.G.S. units. E (the corrosion cell e.m.f.) in volts has been taken as defining the fourth fundamental unit in this system. The complete set of corrosion properties will thus be measured in decimetres, milligrammes, days and volts or in d.m.d.v. units.

Two new quantities are introduced in this table, namely K and ξ , the former defined by

$$K = \frac{\partial C}{\partial E} \dots\dots\dots (1)$$

and the latter by

$$\xi = \frac{\partial \rho}{\partial C} \dots\dots\dots (2)$$

K is thus a measure of the capacity of the system for the corrodant, or the quantity in solution required to change the overall cell e.m.f. by one volt; and ξ , a dimensionless quantity, is defined as the change in density produced by unit change in the concentration of the corrodant. The diffusivity term D_c is simply defined by analogy with the thermometric conductivity or thermal diffusivity.

EXPERIMENTAL MEASUREMENTS ON FORCED CONVECTION.

In these experiments the body of the metal corroded took the form of a cylindrical tube, being part of a pipe system through which the corrodant flowed at a measured rate. The test piece fitted flush into glass pipes of the same diameter so that no eddies were created by any discontinuity in the rate or direction of flow. The test piece was weighed before and after a measured time interval during which the flow rate (Γ) has been maintained constant. From a series of such measurements on any one tube, q could be measured as a function of Γ . Various tubes of copper, brass, phosphor bronze and mild steel of different lengths and diameters were used. The resultant q versus Γ curves were all of the same form. Very low rates of flow produced no increase in the rate of corrosion. Further increase in the flow rate resulted in a sharp increase in the rate of corrosion, but at still higher flow rates the rate of corrosion again became independent of the rate of flow. An increase in corrosion rate with flow rate has been recorded by Hatch and Rice (1945). In all the examples studied the velocity of flow required to give practically a stationary final corrosion rate were well within the region of laminar flow. Figure 1 gives some illustrative results obtained in the study of corrosion of a mild steel tube 10.0 cms. long and 0.33 cm. internal diameter, by a 60/40 acetic acid acetic anhydride mixture; and Figure 2 similar results from a copper tube 15.6 cms. long and 0.454 cm. internal diameter, both at 20° C. The group of curves shown in Figure 3 refer to the corrosion of copper tubes of the various lengths and diameters indicated on the legend, exposed to a 50% aqueous acetic acid solution. The tubes were prepared from a given batch of copper and were given an identical heat treatment and finally quenched in alcohol just before use. The corrosion rates for very fast and very slow rates of flow were independent of the diameters of the tubes. At intermediate rates the shorter and finer tubes corroded relatively faster than the longer and wider ones.

THE PROBLEM OF HEAT LOSS UNDER FORCED CONVECTION.

The problem of the change in heat transmittance (h) with change in the velocity of flow in a pipe has been subject to considerable study and experimental results have been co-ordinated by means of dimensionless quantities.

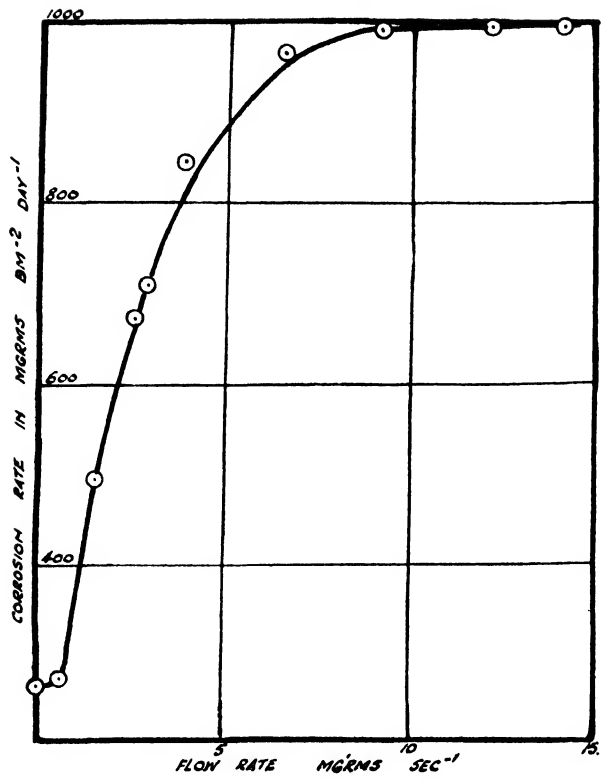


Fig. 1.

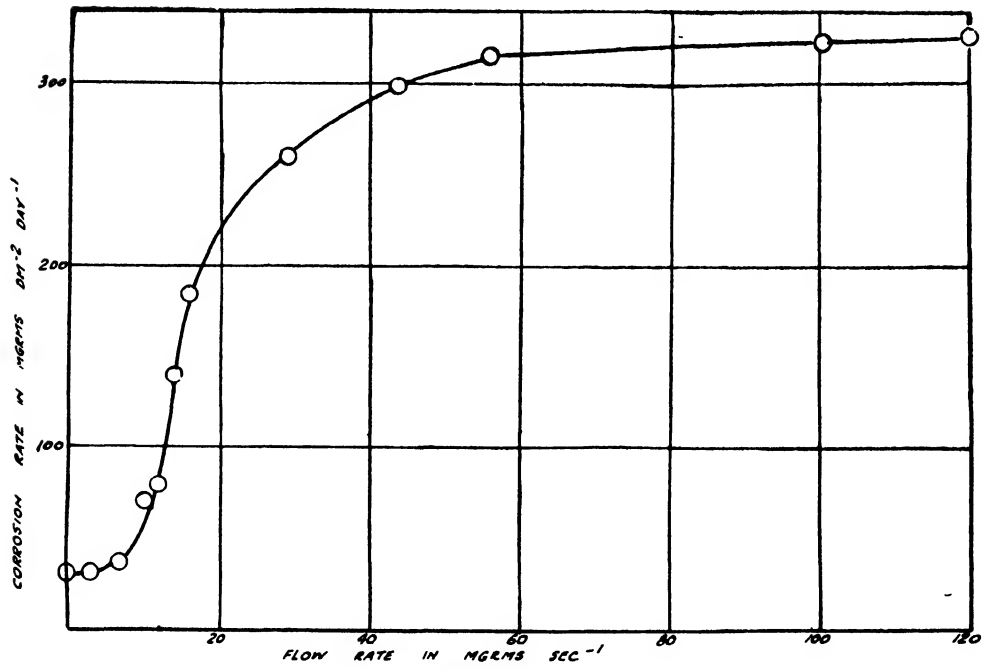


Fig. 2.

For heat transference in the region of laminar flow McAdams (1942) gives the expression

$$\frac{hd}{k\theta} = 2.01 \left(\frac{\Gamma c_p}{kl} \right)^{1/3} \left(\frac{\eta}{\eta_w} \right)^{0.14}, \dots\dots\dots (3)$$

where η is the viscosity of the fluid in the centre of the pipe and η_w that at the

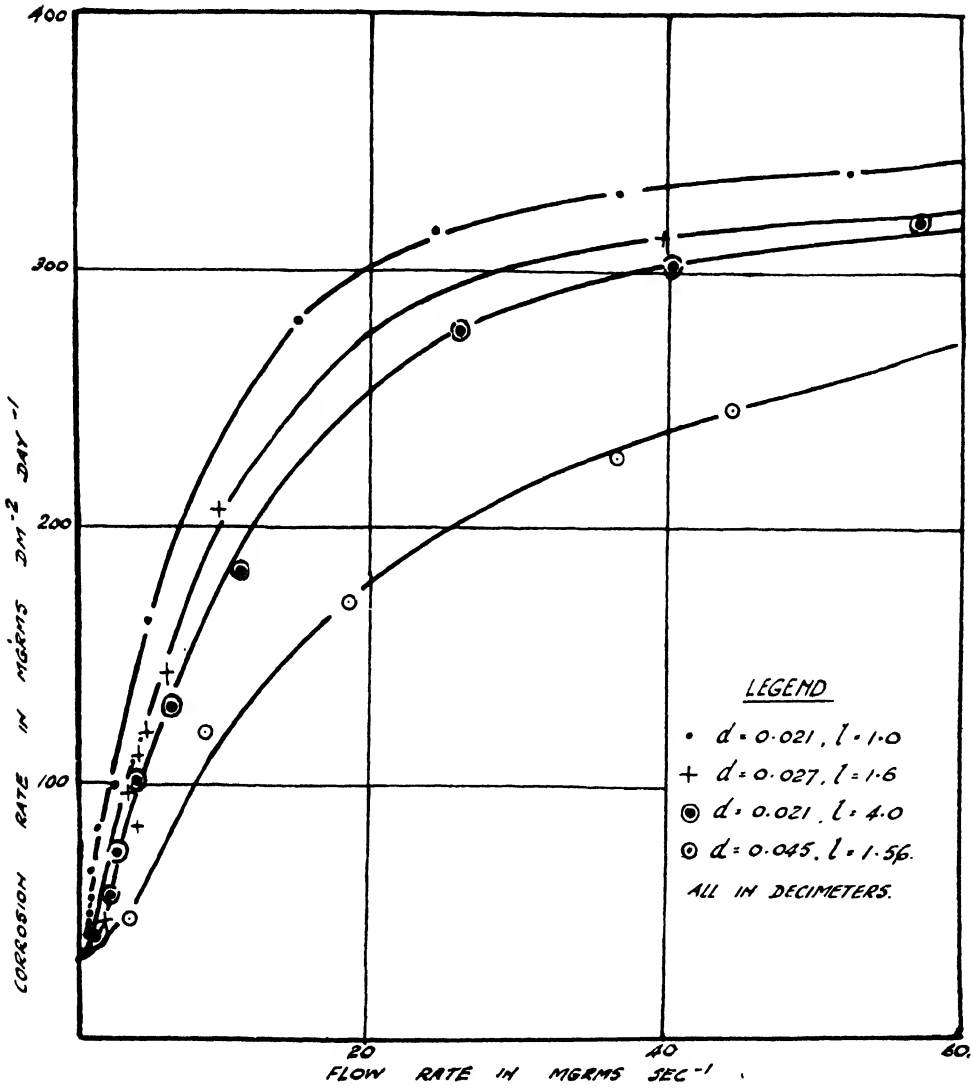


Fig. 3.

walls. The other symbols have the meanings outlined in Table 1. When convection is transporting not heat but the soluble products of corrosion there is no reason why the viscosity at the walls should be significantly different from that at the centre of the pipe. Equation (3) transposed to quantities concerned with corrosion will therefore take the form

$$\frac{qd}{j(1-q/q_0)} = 2.01 \left(\frac{\Gamma K}{j l \rho} \right)^{1/3} E^{1/3} \dots\dots\dots (4)$$

where the symbols again have the meanings given in Table 1. Equation (4) may be rewritten as

$$\frac{1}{q} - \frac{1}{q_0} = 0.498 \left(\frac{d^3 l}{\Gamma} \right)^{1/3} \left(\frac{\rho}{KEj^2} \right)^{1/3}$$

or

$$\frac{\partial \left(\frac{1}{q} \right)}{\partial \left(\frac{d^3 l}{\Gamma} \right)^{1/3}} = 0.498 \left(\frac{\rho}{KEj^2} \right)^{1/3} \dots\dots\dots (5)$$

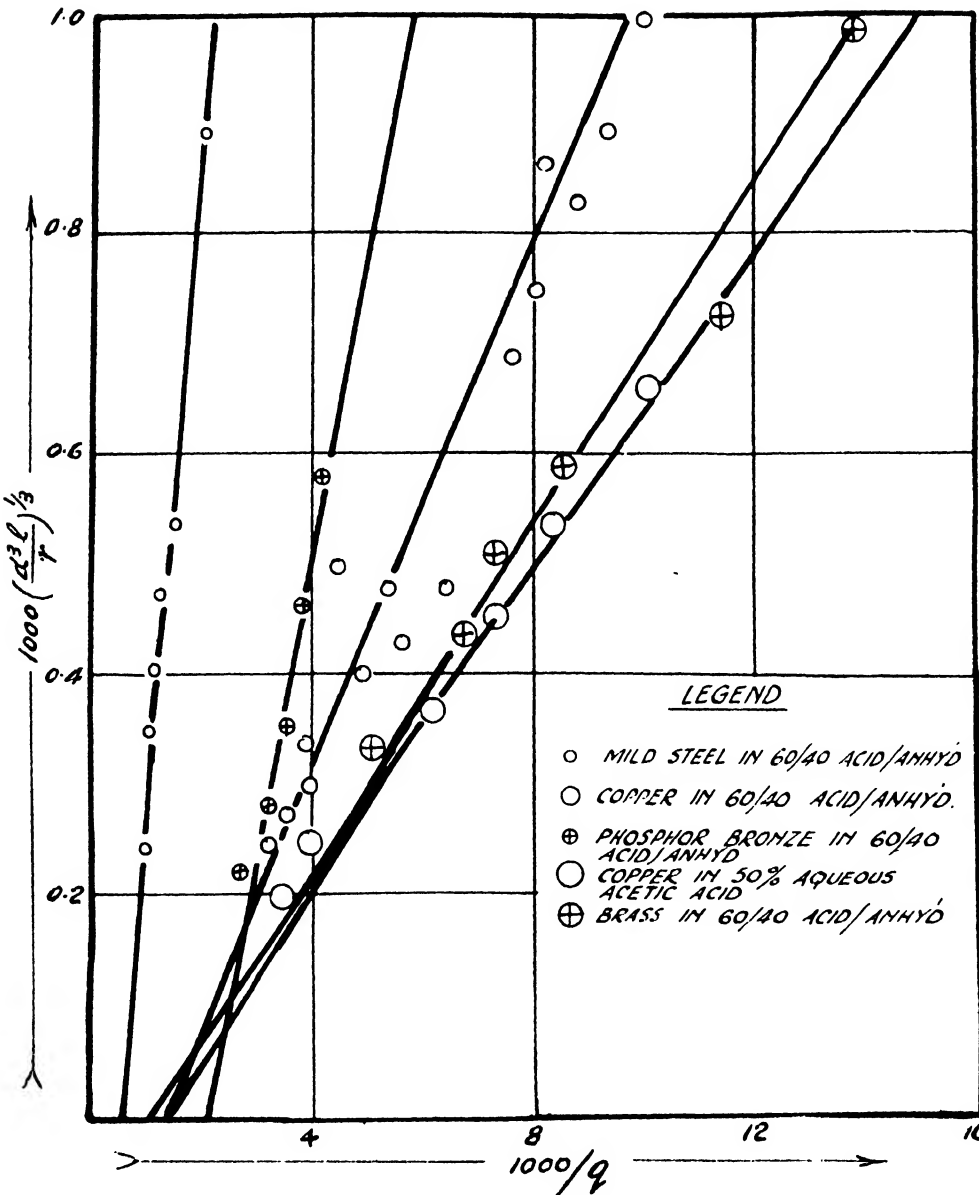


Fig. 4.

So that experimental results may therefore be fitted to this equation by plotting $1/q$ versus $\left(\frac{d^3l}{\Gamma}\right)^{1/3}$. The results treated in this way are shown in Figure 4. The experimental points for each system studied lie on a straight line, giving a positive intercept on the $1/q$ axis. The slopes of these lines are a measure of the quantity $\left(\frac{\rho}{KEj^2}\right)$. Thus we have

$$\left(\frac{\rho}{KEj^2}\right)^{1/3} = 2.01 \frac{\partial\left(\frac{1}{q}\right)}{\partial\left(\frac{d^3l}{\Gamma}\right)^{1/3}} \dots\dots\dots (5a)$$

$= 16.1$ d.m.d.v. units (copper in 60/40 acetic acid-acetic anhydride).
 $= 29.1$ d.m.d.v. units (copper in 50% aqueous acetic).
 $= 3.32$ d.m.d.v. units (mild steel in 60/40 acetic acid-anhydride).
 $= 7.44$ d.m.d.v. units (phosphor bronze in 60/40 acetic acid-anhydride).
 $= 26.1$ d.m.d.v. units (brass in 60/40 acetic acid-anhydride).

The values of the densities ρ in d.m.d.v. units are :

- 1.056×10^6 for 50% aqueous acetic acid and
- 1.060×10^6 for 60/40 acetic acid acetic anhydride.

Using the values of j from the earlier paper, we may now compute the values of the product KE for the five examples above. An independent measurement of E (from over-voltage measurements or from the Gibbs' free energy of the corrosion reaction) is necessary before we can derive the values of the capacity terms K . However, for many purposes the product KE is all that is required. Thus the coefficient of diffusion D_c of the depolarizing agent is related to j and KE by the expression

$$D_c = \frac{j}{KE} \text{ decimetres}^2 \text{ day}^{-1}$$

$$= 1.16 \times 10^{-3} \frac{j}{KE} \text{ cms.}^2 \text{ sec.}^{-1}.$$

Values of KE and D_c computed from the figures above are given in Table 2.

TABLE 2.

| Metal. | Corrodant. | KE in d.m.d.v. Units. | D_c in | |
|-----------------|--|-------------------------------|--------------------|------------------|
| | | | d.m.d.v. Units. | C.G.S. Units. |
| Copper | 50% aqueous acetic. | 1.20 | 5.0 | 0.0058 |
| Copper | 60/40 acetic acid-acetic an- hydride. | 2.3 | 4.6 | 0.0053 |
| Mild steel .. | 60/40 acetic acid-acetic an- hydride. | 10.8 | 4.8 | 0.0056 |
| Brass | 60/40 acetic acid-acetic an- hydride. | 1.5 | 4.1 | 0.0048 |
| Phosphor bronze | 60/40 acetic acid-acetic an- hydride. | 4.2 | 4.3 | 0.0050 |

It will be observed from this table that whereas the values of KE vary practically over a tenfold range the values of the diffusivities are, within the limits of an experimental error accentuated by the act of cubing, constant. It therefore appears that these observations lend support to a suggestion that the same depolarizing agent is concerned in all these cases. The absolute magnitude of the diffusion coefficient is considerably higher than those usually given by liquid systems. Thus Sherwood (1937) claims that the diffusivities of most organic and inorganic matter in liquids lie between 0.3 and 1.5×10^{-5} cms.² sec.⁻¹, or about 3×10^{-3} of the figures estimated above for the diffusivity of the depolarizing agent.

SUMMARY.

The rate of corrosion of metal tubes through which a corrodant liquid is caused to flow has been measured as a function of the rate of flow. The rate of corrosion increases as the flow rate increases but becomes practically stationary when the rate of flow is still quite low.

The variation of the rate of loss of matter with the rate of flow takes the same form as that for the rate of loss of heat from a geometrically similar lagged hot pipe through which a conducting fluid is caused to flow.

The diffusivity of the depolarizing agent, defined as an expression analogous to the thermometric conductivity, proves to be the same for all metals and corrodants studied, and is of the order 5×10^{-3} cms.² sec.⁻¹.

A table is given showing the properties concerned in the convective loss of heat together with the corresponding terms involved in the convective transfer of matter concerned in the process of corrosion.

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THE INFLUENCE OF NATURAL CONVECTION ON THE PROCESS OF CORROSION.

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INTRODUCTION.

Two earlier papers (Bosworth, 1949*a*, 1949*b*) have traced a degree of parallelism between heat loss by conduction and convection and matter loss by corrosion under conditions of forced convection and in circumstances in which all convection currents have been eliminated by the use of guard rings. The present paper extends this study to the consideration of natural convective losses from cylindrical bodies placed horizontally in a corrodant liquid. The convective heat loss from cylindrical bodies such as hot wires or steam pipes immersed in fluids has, on account of its economic importance, been subject to very considerable detailed examination. A fairly complete review of the findings in this field have been given by Lander (1942). For convective heat loss from horizontal cylinders the emittance q is related to the other physical variables by means of the dimensionless equation

$$\frac{qd}{k\theta} = F\left(\frac{d^3 \rho^2 g}{\eta k} \frac{c_p}{\beta} \frac{\theta}{\theta}\right) \dots\dots\dots (1)$$

where the symbols have the meanings given in Table 1 of the previous paper (Bosworth, 1949*b*) and $F(\)$ is a function which has been determined experimentally.

The methods of correlating experimental data expressed by means of equation (1) have been extended by analogy with the problems of the convective loss of matter by evaporation. Thus Sutton (1934), Powell and Griffiths (1939) and Pasquill (1943) have shown that losses by evaporation follows laws analogous to the loss of heat from similarly shaped hot bodies. The convective loss by corrosion, in as much as the rate is controlled by the conveyance of the active constituent to the surface and the removal of the products of reaction by convective currents set up as a result of the density changes produced by the reaction, appears to be quite analogous to the convective loss of water by evaporation with the simple difference that the convective current now flows downwards past the corroding body. If we transpose equation (1) over to properties concerned with corrosion according to Table 1 of the previous paper (Bosworth, 1949*b*) we get

$$\frac{qd}{j(1-q/q_0)} = F\left(\frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}\right) \dots\dots\dots (2)$$

EXPERIMENTAL.

The validity of equation (2) has been tested experimentally by placing a number of cylinders of different metals and different diameters in a horizontal position at a given depth (2 cms.) below the free surface of different corrodant liquids in such a way that the cylindrical and not the end faces could be attacked. After standing in a thermostat for a given time, ranging from 24 to 168 hours, the samples were removed and weighed and the corrosion rates (q) determined. The metals investigated included deoxidized copper, mild steel, phosphor bronze and a brass (37% Zn, 63% Cu).

Of the various factors which occur in equation (2), the values of j (the corrosion conductivity) and q_0 (the maximum corrosion rate) have been determined by experiments on the guard ring equipment (Bosworth, 1949a). The product KE has likewise been determined (for the systems studied) by measurements under conditions of forced convection (Bosworth, 1949b). Figures for η , the viscosity of the corrodant medium, are readily available, so that there remains only the quantity ξ to be determined before equation (2) may be put to an experimental test. This factor may be computed from observations of the density of the corrodant before and after a given quantity of each metal has been dissolved in a known volume. Samples of the corrodant were therefore collected after various measured masses of each metal had dissolved in a known volume and their densities were determined by pycnometer measurements in a constant temperature room.

RESULTS.

The results obtained from the study of corrosion from horizontal cylinders are summarized in Figure 1, in which the corrosion rates for various metals, in each of a number of selected corrodants at 20° and 70°, are plotted against the

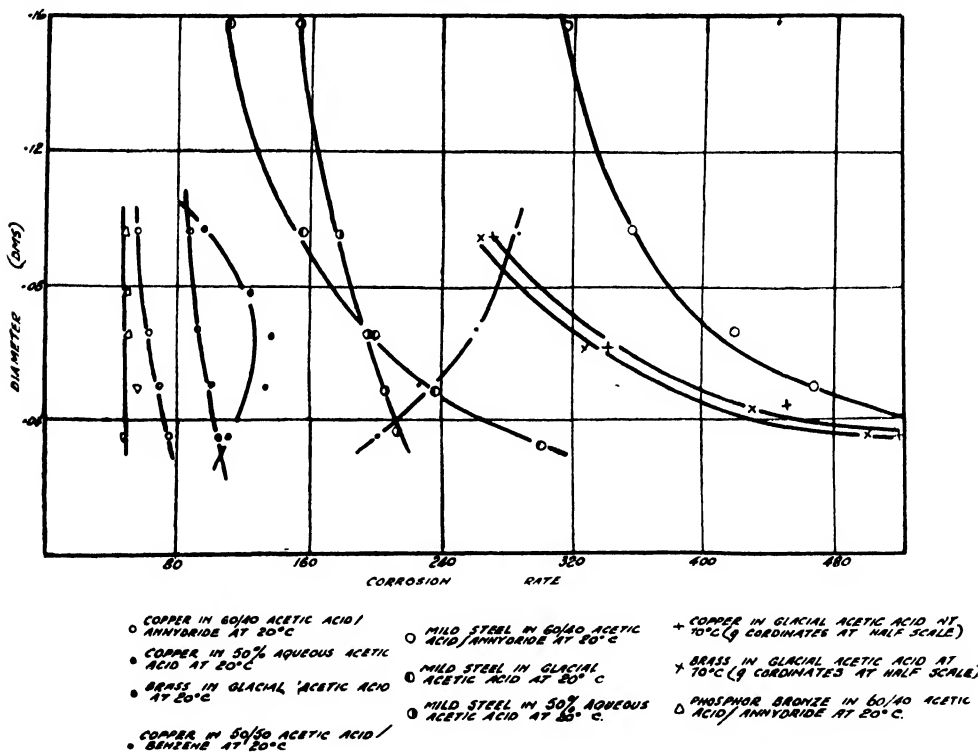


Fig. 1.

diameter of the specimen. In order to present as much data as possible on the one graph the scale for the q (or corrosion rate) axis referring to measurements at 70° C. is half that used for the measurements at 20° C.

It will be observed from the figure that for those systems in which the corrosive action is comparatively mild the rate of corrosion (in units of mass lost per unit area per unit time) varies only slightly with the diameter, and varies in such a way that the rate is somewhat faster for the smaller specimens. For

systems in which the corrosion rate is faster, such as mild steel at 20° C. or the copper alloys at 70° C., the variation of q with d (the diameter) is much more pronounced, so much so that for these systems the product qd (or the mass loss per unit length per unit time) is practically a constant. The one system examined with a very large value of j at room temperature (namely copper in 50% acetic acid 50% benzene) also gave a big variation of q with d , but one in the opposite direction, i.e. one in which the larger specimens corroded relatively faster than the smaller.

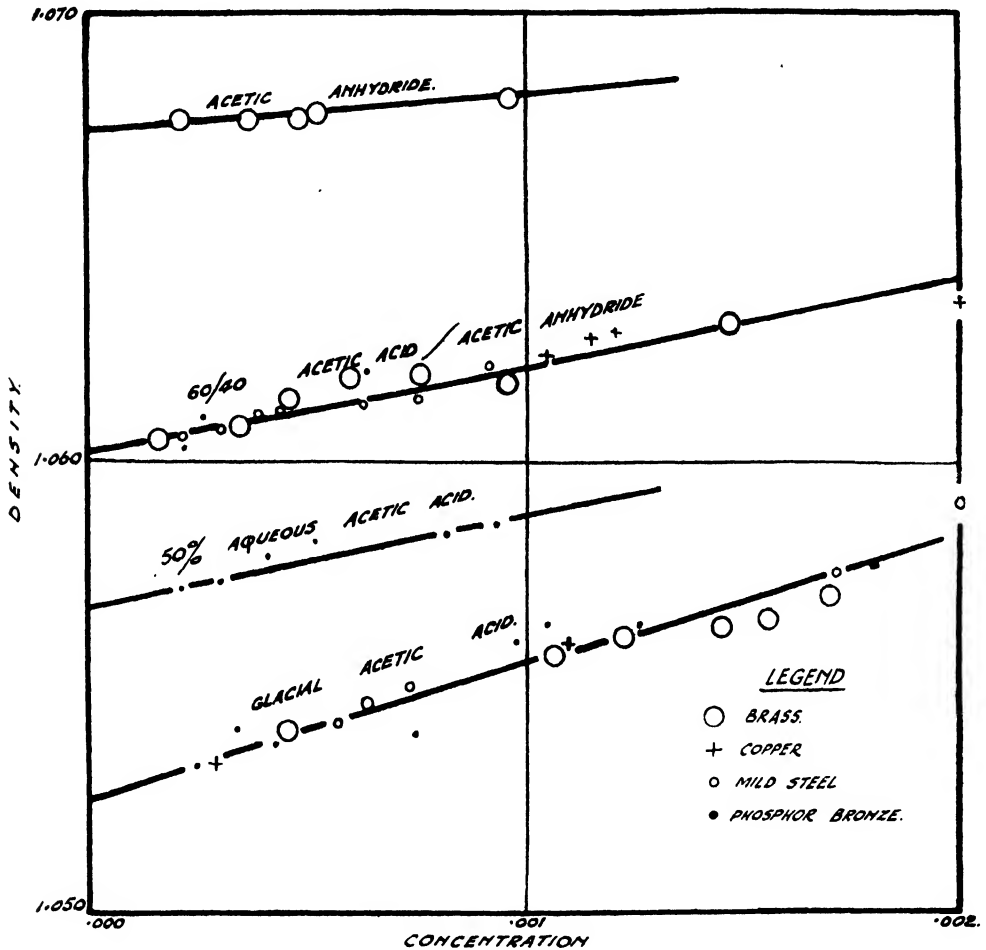
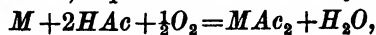


Fig. 2.

The dimensionless quantity ξ referred to above is defined as the ratio of the density change produced to the concentration of corroded metal measured in units of mass per unit volume of corrodant. While some water was formed during the corrosion action, represented chemically by



where M represents any divalent metal; the corrodants examined were hydroscopic in nature and care was necessary in order to prevent the condensation of additional water from the atmosphere with consequent dilution of the corrodant. Figure 2 shows densities plotted against the concentrations for some of the

systems studied. It will be seen that the different metals and alloys studied do not give significantly different results with respect to this property. The different fluids tested do however behave differently, the lower the density of the fluid the more pronounced the density change produced by dissolving a given small quantity of metal in it. The values of ξ from Figure 2, with the associated values of ρ , the original densities of the corrodants, are given in Table 1.

TABLE 1.

| Corrodant. | Density ρ . | ξ . |
|---------------------------------------|------------------|---------|
| Acetic anhydride | 1.0674 | 0.7 |
| 60/40 acetic acid-acetic anhydride .. | 1.0602 | 1.7 |
| 50% aqueous acetic acid | 1.0568 | 2.0 |
| Glacial acetic acid | 1.0524 | 3.0 |
| 50/50 acetic acid-benzene | 0.9475 | 12.0 |

CORRELATION OF RESULTS ON NATURAL CONVECTION.

We have now found, in the case of four of the systems studied, all the data necessary in order to compute the magnitude of both of the dimensionless quantities in equation (2). These systems are: copper in 50% aqueous acetic acid, and copper, mild steel, brass and bronze in the 60/40 acetic acid-acetic anhydride mixture. In Figure 3 the data for these systems, each represented by distinctive points, are shown plotted as

$$\log \frac{qd}{j(1-q/q_0)}$$

versus

$$\log \frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}.$$

The full line shown on the figure is the curve for the corresponding dimensionless quantities involved in the loss of heat from horizontal cylinders by natural convection. This curve was taken from the paper by Lander (1942). The excellent agreement between the points, for the corrosive loss of matter by natural convection; and the curve, for the loss of heat from geometrically similar bodies by thermal convection, is a very clear indication that the phenomena involved are similar and the process which removes the products of corrosion from a surface and brings a continuous supply of the depolarizing agent is essentially the same as that involved in the removal of heat by the natural convection currents.

Data for correlation of all the curves shown on Figure 1 in terms of the dimensionless quantities shown in Figure 3 are not yet complete, mainly because sufficient independent values of KE are not available. However, if we assume that corrosion data would follow the heat convection curve over a wider range than shown above we may make certain interesting deductions the implications of which will be examined in a following paper. It has been shown that, for higher temperature corrosion, the product qd is practically a constant. In heat flow problems the corresponding quantity also becomes practically constant when the right-hand side of equation (1) is made less than about 10^{-4} (Bosworth, 1944). We conclude, then, that the condition $qd = \text{a constant}$ in a corrosion problem means that the right-hand side of equation (2) is very small. This might be effected, for example, by the value of K decreasing with increase in temperature, a fact which becomes significant when an attempt is made to interpret K in terms of the physical and chemical properties of the solution.

CONCLUSIONS.

As a result of the study of mild steel and copper alloys in acetic acid and acetic anhydride mixtures under such physical conditions that the removal of the products of reaction from the corroding surface takes place in a closely defined manner, it is concluded that an analogy may be set up between the rate of matter loss by corrosion on the one hand and the rate of heat loss from a lagged hot body on the other. Further, when the physical variables concerned with each phenomena are expressed as dimensionless products corresponding to the Nusselt number and the product of the Grashof and the Prandtl numbers respectively, the same function expresses the relationship between the parallel sets of dimensionless products applying to both phenomena.

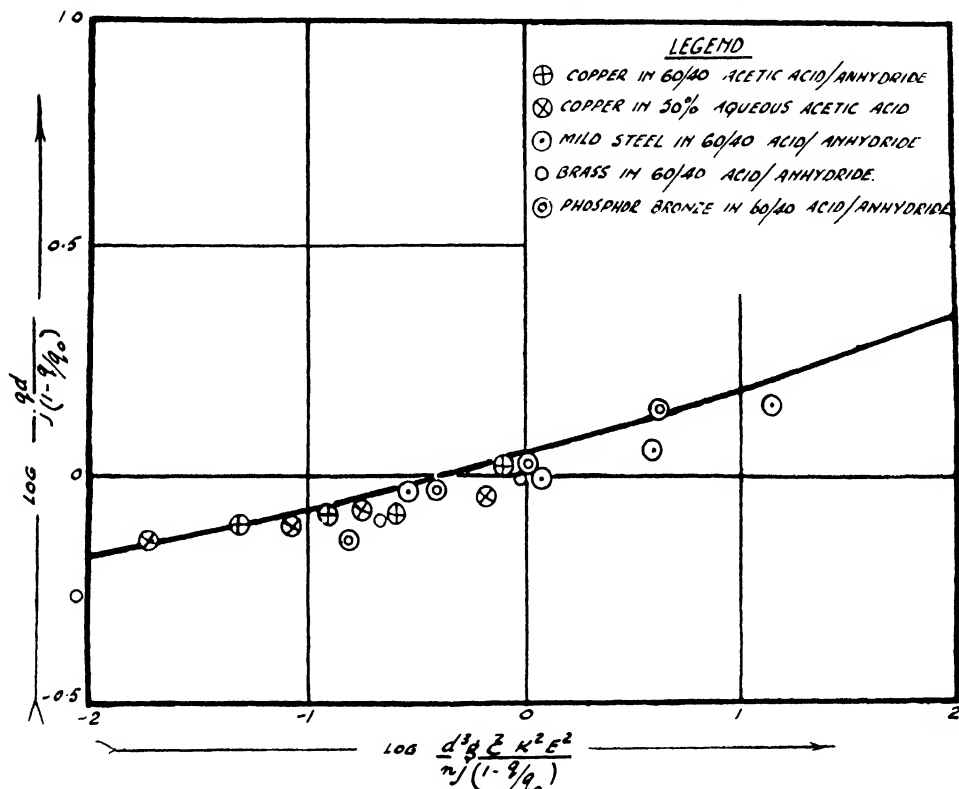


Fig. 3.

This result suggests that a method for estimating the behaviour of large-scale metal members subject to corrosion could be established by setting up an appropriate thermal model. However, it must be emphasized that the principles as developed in these three papers apply at the moment only to a restricted field of corrosion problems—namely to those in which bimetallic corrosion cells are absent and in which the products of corrosion do not form insoluble films and thus give rise to a type of restriction to the flow of matter, of which a counterpart is not realized in the convective flow of heat.

SUMMARY.

The corrosive loss of matter from a metal cylinder immersed horizontally in a corrodant liquid at a constant temperature has been measured for a number

of specimens of different diameters. The metals investigated included mild steel, copper and various copper alloys; the liquids acetic acid and acetic anhydride mixtures. In most cases q (the corrosion rate) tends to increase as d (the diameter) is decreased and in some cases the product qd is practically constant.

When the dimensionless products of the properties involved in corrosion analogous to the Nusselt, Prandtl and Grashof numbers are set up, the functional relationship between them is shown to be the same as that applying to the convective loss of heat from geometrically similar bodies.

It is suggested, therefore, that under certain conditions the use of thermal models could be a useful tool in extrapolating corrosion data from small to large-scale equipment.

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THE FORMATION OF MOBILE AND IMMOBILE FILMS OF OXYGEN ON TUNGSTEN.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

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INTRODUCTION.

The contact potential method of studying the properties of films on metal surfaces has been developed into a tool suitable for both electro-positive and electro-negative films (Bosworth and Rideal, 1937; Bosworth, 1945). Since the contact potential difference between a covered and a bare surface is an easily measurable index of the fraction (θ) of the surface covered, it can be used to record the changes in θ which follow such surface processes as evaporation and condensation. This paper will be devoted to an application of the contact potential method to the study of the condensation of oxygen on tungsten.

An analysis by Roberts (1935, 1938) of the kinetics of adsorption with dissociation of a diatomic gas has shown that condensation proceeds far more slowly if the film formed is mobile than if the film formed is immobile, particularly when the interaction between the adsorbed atoms (or adatoms) is large. For the rate of change of θ (with time) Roberts gave the expression

$$\frac{d\theta}{dt} = \frac{2}{n_s} \frac{\alpha_2 p_2}{\sqrt{2\pi m k T}} \varphi(\theta), \dots\dots\dots (1)$$

where n_s is the number of spaces per unit area available for adsorption.

α is the condensation coefficient.

p is the pressure due to the molecules.

m is the mass of a single (diatomic) molecule.

k is the Boltzmann gas constant,

T is the absolute temperature, and

$\varphi(\theta)$ is a function derived by Roberts.

For an immobile film the function $\varphi(\theta)$ takes the form

$$\varphi(\theta) = 1 - 1.75\theta - 0.3215\theta^2 - 0.0833\theta^3 - 0.0175\theta^5 \dots\dots\dots (2)$$

For a mobile film $\varphi(\theta)$, while practically the same as for the immobile film at low values of θ , decreases much more rapidly as θ increases and, over the higher values of θ , assumes a value which depends on the interaction energy of the adatoms, being the smaller the higher this energy.

The fraction of the surface covered at which $\varphi(\theta)_{\text{mobile}}$ becomes significantly less than the corresponding value of $\varphi(\theta)_{\text{immobile}}$ depends on the lattice arrangement on the surface. If each adsorption space on the surface has four near neighbours the value of θ at which the difference becomes significant is a little less than 0.5. If the adsorption space has six near neighbours, this value of θ is just under 0.33.

Many of the adsorbed films for which the property of surface mobility has been studied have shown immobility at low temperatures and mobility at higher temperatures (Bosworth, 1942). Accordingly it was considered desirable to study the condensation of oxygen on tungsten over a range of temperatures. Any occurrence of appreciable surface migration in times of the order of the

interval between two successive collisions of a gaseous oxygen molecule at the same lattice point should mean a change in the kinetics of the condensation process at a temperature marking the inception of the surface migration.

EXPERIMENTAL.

The apparatus used consisted of a tube for the measurement of contact potential differences of the type already described (Bosworth and Rideal, 1937). A sketch of the apparatus used has been given by Bosworth (1945a). In addition to the normal two crossed tungsten filaments the tube contained a barium oxide coated nickel filament which had been previously heated in an oxygen atmosphere in order to convert the coating into BaO_2 . When all the parts had been assembled the tube was exhausted, using a two-stage mercury diffusion pump; and all the metal parts, with the exception of the BaO_2 coated filament, were thoroughly outgassed. Sodium metal was then distilled into the vessel in order to produce a mirror on the glass walls, but not on the metal filaments, which were maintained hot during this process. The vessel was finally sealed off under vacuum.

Any desired oxygen pressure could now be maintained in the tube first by immersion in a liquid air bath and then by heating the BaO_2 coated filament with a known current. This produced an evolution of oxygen at a fixed rate; and since every oxygen molecule striking the cooled walls was immobilized by the sodium film, this also resulted in a fixed oxygen pressure which could be varied at will by varying the heating current to the oxygen-emitting filament.

The current-temperature curves for the two cross filaments were obtained by measuring the current-resistance characteristics at temperatures below 1000°K. , and the current-brightness temperature curve (using an optical pyrometer) in the higher temperature range.

Contact potential differences were obtained by drawing the infrasaturation curve from emitter filament to collector filament. The former was maintained at a fixed temperature of the order 2500°K. , while the latter was taken through a series of small external potential differences (from -2 volts to $+1$ volt) with respect to the central point of the hot filament. A string galvanometer with recording camera was used to follow rapid changes in the contact p.d. The method of working was as follows: A stable equilibrium film was allowed to build up on the collector filament and a series of snapshots of the galvanometer string taken with the camera, over a range of external applied potentials. A suitable external potential was then selected so that the expected curve for the variation of the emission with change in the contact potential difference consequent on a change in the chemical nature of the surface film should lie wholly within the range of the camera. The oxygen pressure was adjusted to the desired figure by means of the current through the barium dioxide source and the collector filament was heated to 2200°C. to clean it. The camera drive was then set going. The collector filament temperature was then dropped to the figure at which condensation was to be studied by suddenly changing the heating current. Initially rapid changes in galvanometer current occurred and the camera was stopped when this change became substantially constant. Further records were then obtained by reflashng the collector filament and then dropping the temperature to some other point in the condensing range (90 to 1000°K.). As explained above, changes in the oxygen pressure could be effected by changing the heating current on the BaO_2 source. The relative pressures attained could be measured from the slope of the initial part of the condensation curve or from the whole of the condensation curve at 90°K. , at which temperature condensation follows entirely the mechanism associated with the immobile film.

EXPERIMENTAL RESULTS.

The results accruing from the various experimental runs were collected in the first instance in the form of records of the infrasaturation emission versus time curves for the various experimental conditions studied. Using the known current-volts characteristic of the assembly, the curves were first changed to contact p.d. versus time curves and then by means of the relationship between the contact p.d. and θ found earlier for oxygen on tungsten films (Bosworth, 1945*b*) were finally converted to θ versus time curves. Some illustrative curves of this nature are shown in Figures 1 and 2.

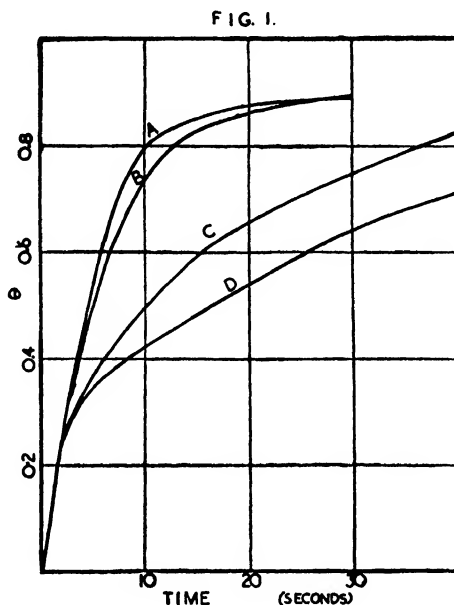


Figure 1 refers to condensation at a fixed oxygen pressure of 1.1×10^{-6} mms. of mercury and at a series of different temperatures. Curve A records the process of condensation at 90°K. , curve B condensation at 540°K. , curve C at 690°K. , and curve D at 920°K.

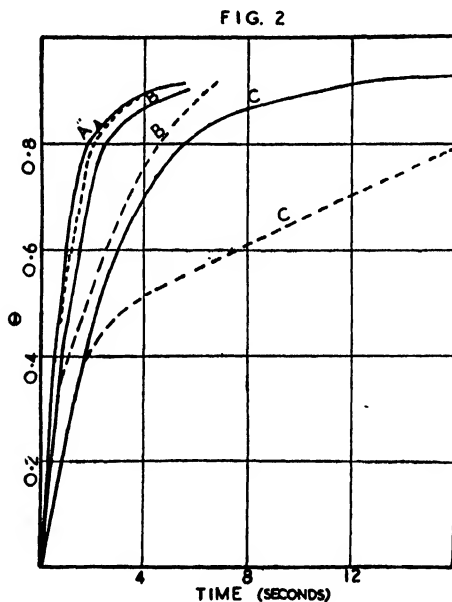
Figure 2 refers to condensation at a pair of fixed temperatures, one each in the mobile and the immobile range, and at a series of different oxygen pressures. Curves AA record condensation at a pressure of 7.4×10^{-6} mms. of mercury, curves BB at 4.4×10^{-6} mms., and curves CC at 2.0×10^{-6} mms. In each case the heavy lines refer to condensation at 90°K. and the broken lines to condensation at 830°K.

It will be observed that at about $\theta = 0.5$ or a little less the condensation proceeds the more slowly the higher the temperature at any fixed pressure, and more than proportionally slowly the lower the pressure at any fixed temperature. These results are not such as would be expected from the simple Roberts' theory.

THEORY.

In the Roberts' theory for the condensation of a completely mobile film the condensation proceeds the more slowly the lower the quantity (η) or $e^{-V/kT}$, in which V is the interaction energy between a pair of atoms on the surface. V varies only slowly with the temperature. Accordingly η is expected to increase with an increase in temperature. Condensation on a completely mobile film is

thus expected to proceed more rapidly at higher temperatures and this, as pointed out above, is not observed. However, a sudden onset of a mobility on the surface akin to a type of two-dimensional melting is also a phenomenon which has only been recorded in a few special cases. Much more usually the process of acquiring a state of surface mobility is more akin to a two-dimensional vaporization. On the picture given by Lennard Jones (1937) the mobile adatom is in a certain state of high energy and remains in that state for a finite time before being deactivated to return to the normal state of being fixed to a given lattice point. In this static condition the adatom remains, on the average, for a much longer time interval before being reactivated to the mobile condition. At any given instant the number of adatoms in the mobile state is only a small fraction of the total number. In considering the effect of activated mobility on the rate of condensation it would appear that the important factor is the probability of a given adsorbed atom migrating to a neighbouring lattice point before that point suffers a collision from a component atom of a gaseous molecule. Higher surface temperatures are associated with more frequent activations to the mobile state and therefore at such temperatures the film behaves as though it



were more completely mobile in the Roberts sense. Again at lower pressures the time intervals between successive collisions become longer, so that the film also behaves as though it were more mobile.

At any fixed temperature and pressure the rate of condensation of a (truly) mobile film depends on the quantity η .

$$\eta = e^{-V/kT},$$

where V is the interaction energy between a pair of adatoms. Above a value of θ of about 0.5 the rate of condensation becomes practically zero when η is small. For oxygen on tungsten films we may estimate V from the figures given by Bosworth (1945) for the heat of evaporation of oxygen from nearly bare and from completely covered surfaces. These heats are respectively 154,000 and 66,000 calories per gramme molecule. Since each lattice point on the 110 surface plane has six almost equidistant neighbours, and further since dipole interaction as calculated by the Topping equation is negligible in comparison

with the total interaction, we may neglect all interaction other than that between near neighbours and write

$$V = \frac{154,000 - 66,000}{6} \\ = 14,700 \text{ calories per gramme molecule.}$$

For a temperature of 750°K. , therefore,

$$\eta \text{ becomes } 0.000068,$$

at which figure the value of $\varphi(\theta)_{\text{mobile}}$ becomes very small in comparison with $\varphi(\theta)_{\text{immobile}}$.

We are now in a position to attempt a computation, from the observed rates of condensation, of a number of adatoms which become mobile in a given time. Let $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$ represent the rate of growth of the film calculated from the theory of immobile condensations for given conditions of θ , temperature and external pressure and let $\left(\frac{d\theta}{dt}\right)_{\text{obs.}}$ be the actual observed rate of growth under the given conditions. In addition to the variables which enter into the determination of $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$ the observed rate of condensation also depends on the state of distribution of the adatoms on the surface at the moment when further condensation takes place. This distribution of the adatoms on the surface may be characterized by two limiting states; a state α in which every atom is attached at the point at which it made the initial collision with the surface and a state β in which surface spreading forces have attained equilibrium with thermal agitation. Condensation on a surface in state α will proceed at the rate $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$. Condensation on a surface in state β (provided $\theta > 0.5$) will proceed at a rate which may be taken as negligibly small in comparison with $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$. Surface migration results in a change from the state α to the state β , and will be assumed to follow a "unimolecular" law, viz.

$$\frac{da}{dt} = -\alpha a$$

or

$$a = 1 - e^{-\alpha t_1}$$

where a represents the fraction of the covered surface in the state α , and t_1 is effectively the time elapsing between two successive collisions at two neighbouring lattice points on the surface. This time depends on the rate at which gaseous molecules impinge effectively on the surface. For immobile condensation the data of Roberts shows that the integral

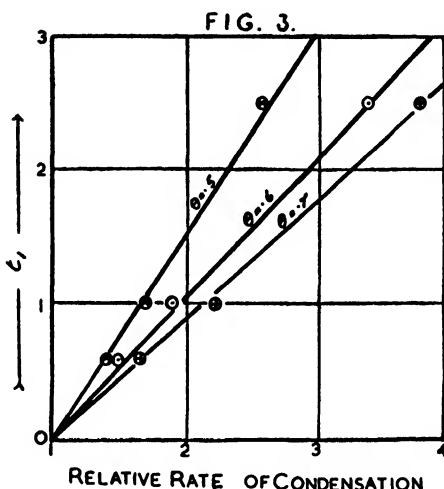
$$\int_0^\theta \frac{d\theta}{\varphi(\theta)}$$

attains the value of 1.0 at $\theta = 0.52$. Accordingly we take for t_1 the time taken for the film to build up from zero concentration to $\theta = 0.52$ under the given external conditions and with the film immobile, i.e. condensation at low temperature.

We may now write for the rate of condensation

$$\begin{aligned}\left(\frac{d\theta}{dt}\right)_{\text{obs.}} &= a \left(\frac{d\theta}{dt}\right)_{\text{im.}} \\ &= (1 - e^{-\kappa t_1}) \left(\frac{d\theta}{dt}\right)_{\text{im.}} \\ &\cong \kappa t_1 \left(\frac{d\theta}{dt}\right)_{\text{im.}},\end{aligned}$$

so long as $\left(\frac{d\theta}{dt}\right)_{\text{obs.}}$ is not of a different order of magnitude to $\left(\frac{d\theta}{dt}\right)_{\text{im.}}$. Thus



we have for the relative rates of condensation

$$\left(\frac{d\theta}{dt}\right)_{\text{obs.}} / \left(\frac{d\theta}{dt}\right)_{\text{im.}} = \kappa t_1.$$

The value of t_1 may be read off from the curves shown on Figure 2 for the three different pressures employed. A plot of $\left(\frac{d\theta}{dt}\right)_{\text{obs.}} / \left(\frac{d\theta}{dt}\right)_{\text{im.}}$ versus t_1 is given in Figure 3 for the three different values of θ , viz. 0.5, 0.6 and 0.7 at 830° K. These points fall on satisfactory straight lines passing through the origin. From the slopes the values of κ may be read off. The values thus obtained are :

At $\theta=0.5$, $T=830^\circ$ K., $\kappa=0.66$ reciprocal seconds.

At $\theta=0.6$, $T=830^\circ$ K., $\kappa=0.95$ reciprocal seconds.

At $\theta=0.7$, $T=830^\circ$ K., $\kappa=1.28$ reciprocal seconds.

CALCULATION OF THE DIFFUSION COEFFICIENTS.

The values of κ deduced above may be taken as measures of the times elapsing between successive activations of the same adatom to the mobile state, and thus may be related to the coefficients of surface diffusion (D) by the expression

$$D = \frac{1}{2} \kappa \lambda^2,$$

where λ is the mean free path of the diffusing adatom and may be taken as the distance between two neighbouring points on the surface lattice. With the

high interaction energy characteristic of the oxygen on tungsten films it is unlikely that a mobile adatom will move over several lattice points before deactivation. Once it has moved out of the range of immediate neighbours of any other adatom it is practically in a uniform field. Thus we have for the diffusion coefficient of oxygen on tungsten

$$D = 3.7 \times 10^{-16} \kappa \text{ cms.}^2 \text{ sec.}^{-1}.$$

At 830° K. the values of D are thus :

For $\theta = 0.5$, $D = 2.45 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$.

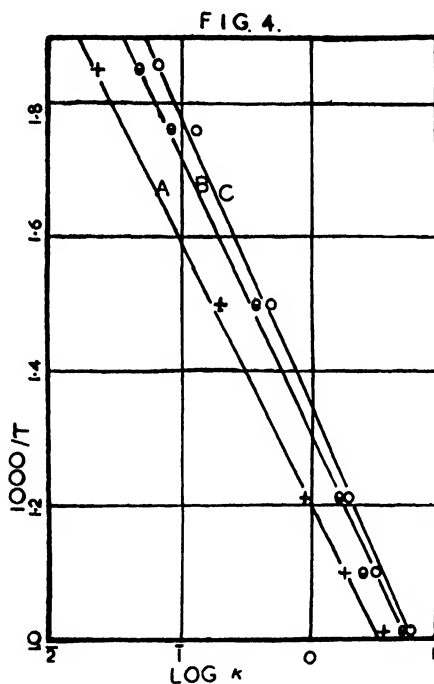
For $\theta = 0.6$, $D = 3.5 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$, and

For $\theta = 0.7$, $D = 4.8 \times 10^{-16} \text{ cms.}^2 \text{ sec.}^{-1}$.

From other measurements of κ it is possible to calculate D over a range of temperatures and values of θ . For an activated process we expect D to vary with temperature according to a relation

$$D = D_0 e^{-b/T}$$

where D_0 is a constant and b is a measure of the activation energy concerned. Some curves showing $\log \kappa$ plotted against $1000/T$ are given in Figure 4. Curve A



refers to $\theta = 0.4$, curve B to $\theta = 0.5$, and curve C to $\theta = 0.6$. Values of the activation energy computed from the slopes of these curves are :

For $\theta = 0.4$, activation energy 0.52 electron volts.

For $\theta = 0.5$, activation energy 0.50 electron volts.

For $\theta = 0.6$, activation energy 0.47 electron volts.

For $\theta = 0.8$, activation energy 0.46 electron volts.

These figures for the activation energy for surface migration are only a small fraction of the corresponding figures for the heats of vaporization for these same films.

SUMMARY.

The contact potential difference has been used to study the condensation of oxygen on tungsten. At low temperatures the process follows the kinetics expected by the Roberts' theory of condensation with dissociation as an immobile film. At higher temperatures the condensation (once θ has exceeded a value of about 0.4) proceeds the more slowly the higher the temperature or the lower the pressure. This is interpreted as due to the activation of some of the adsorbed oxygen atoms to a mobile state which proceeds the more rapidly the higher the temperature and the more completely the lower the pressure.

Calculation of the surface diffusion coefficient at 830° K. gives a figure of 2.5×10^{-16} cms.² sec.⁻¹ at $\theta=0.5$, increasing with increase in θ and an activation energy of 0.50 electron volts for $\theta=0.5$, this time decreasing with increase in θ .

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A NOTE ON THE SIGMA PHENOMENON.

By R. C. L. BOSWORTH, Ph.D., D.Sc., F.Inst.P.

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I. INTRODUCTION.

The sigma phenomenon, which has been described in some detail by Scott Blair (1938, 1944), is apparently of wide occurrence in the flow of semi-fluid pastes and slurries. In the method of studying the flow of such systems introduced by Schofield and Scott Blair (1930, 1931, 1935) we plot the mean velocity of the flow (U) against the stress (τ) at the wall. If the one system is studied in a series of pipes of different diameters we get a series of straight lines, one for each tube diameter. Let us call the slope of these lines ($dU/d\tau$) a quantity σ , and then proceed to plot σ against R , the radius of the tube. Were the fluid system studied to be Newtonian in behaviour, it would follow that the resultant plot would be a straight line passing through the origin and having a slope ($d\sigma/dR$) equal to $1/4 \eta$, with η the viscosity. For systems exhibiting the sigma phenomenon the σ versus R plots are reasonable straight lines, but they do not pass through the origin, but instead give a positive slope σ_0 on the σ axis. Thus for such systems we have

$$\frac{dU}{d\tau} = \sigma_0 + \frac{R}{4\eta} \dots\dots\dots (1)$$

In a paper by the author (Bosworth, 1947) it was shown that this equation had a form resembling that for the flow of a gas in a capillary at such a low pressure that slip flow was occurring, and it was further suggested that similar mechanisms for the transport of momentum from the fluid to the walls was operative. The peculiar properties of gas flow at low pressure are attributable to the fact that the carriers of momentum (viz. the moving molecules) travel through the system with mean free paths which are of the same order of size as the diameter of the tubes concerned. In seeking a similar mechanism for the transport of momentum in a semi-liquid slurry at atmospheric pressure it was suggested that the class of hypersonic longitudinal waves in the oscillatory motion into which the Debye theory of specific heats breaks up the thermal motion of condensed matter might contribute the momentum carriers with the long mean free paths. It will be the object of this paper to make an estimate of the magnitude of the sigma phenomenon in terms of the Debye distribution of frequencies. A similar estimate by the author (Bosworth, 1948) of the magnitude of the viscosity of normal liquids interpreted as a momentum transfer by transverse waves with mean free paths equal to the mean distance between two "holes" in the liquid has met with moderate success and will be used as a basis for the present calculation.

II. DERIVATION OF THE INTENSITY OF THE MOMENTUM FLOW.

Following the practice adopted in the earlier papers we will refer to the stream of acoustical radiation as a stream of "phonons" carrying quanta of energy and momentum given by the quantum rule. The energy per unit volume

dE associated with longitudinal waves of frequency lying between ν and $\nu + d\nu$ is given by

$$dE = \frac{4\pi h}{c_1^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \dots\dots\dots (2)$$

where c_1 is the velocity of propagation of the longitudinal waves. The number of phonons dn_p per unit volume derived from longitudinal waves in the frequency range ν to $\nu + d\nu$ (or phonons of class B) is expressed by the relationship

$$dn_p = \frac{4\pi}{c_1^3} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \dots\dots\dots (3)$$

The density of these same phonons ($d\rho_p$) is likewise given by

$$d\rho_p = \frac{4\pi h}{c_1^5} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \dots\dots\dots (4)$$

While the number of phonons of class B striking unit area of the wall in unit time is

$$\frac{1}{4} dn_p c_1, \text{ or } \frac{\pi}{c_1^2} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}$$

A like number of phonons will leave the unit area of the wall in unit time in directions which are distributed according to the cosine law. A certain fraction

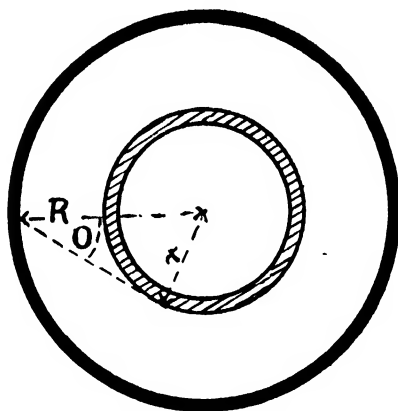


Fig. 1.

of that number will cross the surface of an inner cylinder of radius r . If R is the inner radius of the pipe (Figure 1) then phonons from any given point on the wall will cross the inner cylinder so long as they make an angle θ with the normal which is less than $\arcsin r/R$, in a plane normal to the direction of flow.

The fraction crossing the inner cylinder is thus

$$\int_0^{\arcsin r/R} \cos \theta d\theta = r/R.$$

If α is the absorption coefficient the number of phonons in unit time and from unit wall area which are absorbed between the radii r and $r + dr$ (the shaded area in Figure 1) is then

$$\frac{\pi}{c_1^2} \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1} \cdot \frac{r}{R} \cdot e^{-\alpha(R-r)} \alpha dr.$$

Let now u be the local velocity of flow of the zone of fluid represented by the shaded area. Generally u is a function of r . The momentum flow from unit area of the wall to an area r/R of the shaded zone and due to the phonons of class B now becomes

$$\frac{\pi}{c_1^4} \frac{u h \nu^3 d\nu}{e^{h\nu/kT} - 1} \frac{r}{R} e^{-\alpha(R-r)\alpha dr}.$$

The total momentum flow to the shaded area carried by all the phonons arising from longitudinal waves thus becomes

$$\frac{\pi u r e^{-\alpha(R-r)\alpha dr}}{R c_1^4} \int_0^{\nu_0} \frac{h \nu^3 d\nu}{e^{h\nu/kT} - 1} \dots\dots\dots (5)$$

where ν_0 is the limiting Debye frequency. For all temperatures considerably in excess of the Debye characteristic temperature $\frac{h\nu_0}{k}$ we may write approximately

$$e^{h\nu/kT} - 1 = h\nu/kT,$$

so that expression (5) becomes

$$\frac{\pi r e^{-\alpha(R-r)\alpha dr}}{R c_1^4} \frac{u k T \alpha dr}{3} \frac{\nu_0^3}{3} \dots\dots\dots (6)$$

But now ν_0 is related to the number N of molecules in unit volume by

$$\nu_0^3 = \frac{9N}{4\pi} \frac{1}{\left(\frac{1}{c_l^3} - \frac{2}{c_t^3}\right)}, \dots\dots\dots (7)$$

where c_t is the velocity of propagation of the transverse hypersonic waves. As in the earlier paper, we assume that the Cauchy-Poisson relation holds between c_l and c_t , namely that

$$5c_t^2 = 3c_l^2 \dots\dots\dots (8)$$

which on substitution in equation (7) gives

$$\nu_0^3 = 0.1886 \frac{9}{4\pi} N c_l^3 \dots\dots\dots (9)$$

and this, on substitution in expression (6), gives for the momentum transferred per unit time to the shaded area

$$0.1414 \frac{u e^{-\alpha(R-r)\alpha dr}}{R} \frac{N k T}{c_l}.$$

This momentum flow yields a contribution ($d\tau$) to the stress exerted by the fluid on the walls, namely

$$d\tau = 0.1414 \frac{u N k T}{c_l} \alpha e^{-\alpha(R-r)\alpha dr} \dots\dots\dots (10)$$

The total stress on the walls due to the longitudinal waves becomes

$$\tau = 0.1414 \frac{\alpha k T N}{c_l} \int_0^R u e^{-\alpha(R-r)\alpha dr} \dots\dots\dots (11)$$

Whenever sigma phenomena are in evidence there occurs considerable slip at the walls, thus u varies relatively slowly throughout the pipe except in the immediate vicinity of the walls. Under such conditions we may, without sensible error, take u outside the integral sign in equation (11) and replace it by U , the average velocity of flow in the pipe. Then we get

$$\tau = 0.1414 \frac{\alpha U N k T}{c_l} \int_0^R e^{-\alpha(R-r)\alpha dr}$$

$$=0.1414 \frac{UNkT}{c_1} e^{-\alpha R} \dots\dots\dots (12)$$

as our final expression for the contribution to the stress on the wall due to the collision of photons originating from longitudinal waves.

III. THE MAGNITUDE OF σ_0 .

On differentiation of equation (12) we obtain

$$\frac{dU}{d\tau} = \frac{7.07c_1}{NkT} e^{\alpha R} \dots\dots\dots (13)$$

Now from equation (1) we have for σ_0

$$\begin{aligned} \sigma_0 &= \lim_{R \rightarrow 0} \frac{dU}{d\tau} \\ &= \frac{7.07c_1}{NkT} \end{aligned}$$

But since N is N/V where N is the Avogadro number and V is the molecular volume, and further since Nk is R , the ordinary gas constant, we get finally

$$\sigma_0 = 7.07 \frac{Vc_1}{RT} \dots\dots\dots (15)$$

For aqueous solutions c_1 is of the order 1.5×10^5 cms. sec.⁻¹ and at room temperature RT is 2.5×10^{10} ergs. Accordingly, for such solutions we have for σ_0 the approximate value

$$\sigma_0 = 4.24 \times 10^{-5} V \text{ cms.}^3 \text{ secs.}^{-1} \text{ dynes}^{-1} \dots\dots\dots (16)$$

This estimated value of σ_0 may be compared with the experimental values of Schofield and Scott Blair (1930) for various aqueous pastes. Such a comparison would enable V , the effective molecular volume of the pastes, to be computed. In the table below the experimental values of σ_0 and the estimated values of V obtained therefrom are given in tabular form.

TABLE I.
Effective Molecular Volumes Estimated from the Sigma Phenomenon.
(Data of Schofield and Scott Blair.)

| Paste. | Percentage Solids. | σ_0 (cms. ³ sec. ⁻¹ dynes ⁻¹). | V (Litres). |
|--------------------------|--------------------|--|---------------|
| Clay | 2.36 | 0.33 | 7.7 |
| Kaolin | 37.2 | 0.11 | 2.6 |
| Plaster of Paris | 5.8 | 0.017 | 0.40 |
| Barytes | 43.5 | 0.015 | 0.35 |
| Subsoil | 33.5 | 0.0055 | 0.13 |

These molecular volumes are very large and are more nearly appropriate to a gaseous rather than a liquid system. To the effusive transport of momentum resulting in the sigma phenomenon these slurries thus act as solutions which are very dilute on the molar basis.

SUMMARY.

The suggestion that the sigma phenomenon observed in the flow of certain slurries is due to the transport of momentum to the walls by the acoustical vibrations into which the Debye theory resolves the thermal energy of the molecules is examined quantitatively. It is shown, subject to the assumptions

that the system is far above its Debye temperature and that the ratio of the velocities of the longitudinal and the transverse waves takes the Cauchy-Poisson value, that the value of σ_0 is given by

$$\sigma_0 = 7.07 V c_l / RT,$$

where c_l is the velocity of the longitudinal hypersonic waves and V is the effective molar volume of the slurry. Comparison of this equation with the measurements of Schofield and Scott Blair shows that V has a value of the order of a litre.

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A NOTE ON THE ESSENTIAL OIL OF *BACKHOUSIA ANISATA* VICKERY AND THE OCCURRENCE OF ANETHOLE.

By H. H. G. MCKERN, A.A.C.I.

Manuscript received, January 21, 1949. Read, April 6, 1949.

Although specimens from the myrtaceous tree *Backhousia anisata* Vickery, indigenous to the north coast of New South Wales, were collected as long ago as 1910, it has been confused with *Eugenia ventenatii*, and its taxonomic position was not established until recently by Vickery (1941).

On account of the strong aniseed-like odour of the crushed foliage it has received the vernacular name of "Aniseed Tree", and this observation has prompted officers of the Forestry Commission of New South Wales to enquire into the economic value of the oil as a possible substitute for anise oil. This Institution has undertaken the examination of the oil obtainable from this species, and since a preliminary investigation shows promise of commercial value it has been decided to publish the results hitherto obtained. When further supplies of material become available, a more detailed examination of the oil will be made.

The examination so far shows that the foliage of this tree yields on steam-distillation 0.5% of a pale yellow oil strongly resembling anise oil of commerce in respect both to odour and taste. The principal component of the oil is anethole (*p*-propenyl anisole), present to the extent of about 60%, as compared with about 80% for anise oil. However, it is considered that by rectification or by freezing, a commercial equivalent of anise oil could be prepared, and would provide a local source of anethole. The oil of *B. anisata* is considered by the author to be far superior to fennel oil.

EXPERIMENTAL.

Samples of foliage were supplied by the Forestry Commission of N.S.W. Two collections were made, one, received 4/7/46, from one restricted locality in the Bellenger River area of New South Wales; the other, received 11/11/46, was made up of foliage from three different and separated localities in the same area—Buffer Creek, Pine Creek and Kalang—the purpose of the second sample being to determine if the oil of this species is reasonably constant in composition to justify commercial exploitation.

Both samples consisted of leaves and terminal branchlets cut as for commercial distillation, and on steam-distillation they both yielded 0.5% of a pale yellow mobile oil, lighter than water and having a sweet taste and pronounced anethole-like odour. The oil froze readily to a crystalline mass on cooling in ice-water. The oils had the characteristics shown in the following table; figures for the British Pharmacopœia specification for anise oil being given for comparison.

Preparation and Characterization of the Anethole.

Essential oil of *B. anisata* (47 g.) was frozen by cooling to about +5°. The crystalline mass was transferred to a chilled porous tile and pressed. By repetition of this process, 24 g. of white

| | 4/7/46 Sample. | 11/11/46 Sample. | 1932 B.P. Specifications. (Anise Oil). |
|---|----------------------|----------------------|--|
| Specific gravity at 20°/15.5° .. | 0.9826 | 0.9806 | 0.980 to 0.994 |
| Refractive index, at 20° | 1.5535 | 1.5489 | 1.553 to 1.560 |
| Optical rotation, 100 mm. tube .. | -1.15° | -1.88° | -2° to +1° |
| Freezing point | 14.5° | 12.0° | Not below 15° |
| Melting point | 15.2° | 13.2° | Not below 17° |
| Solubility in 90% V/V alcohol .. | Soluble in 1 vol. | Soluble in 1 vol. | Not more than 3 vols. |
| Ester number, mg. KOH per gramme | — | 15.4 | — |
| Ester number, mg. KOH/g, after acetylation | — | 87.6 | — |

crystals were obtained, melting at 21°–22° to a colourless oil of powerful anethole odour and taste, and having the following characters :

| | | | | | |
|---------------|----|----|----|----|-----------|
| d_{15}^{15} | .. | .. | .. | .. | 0.9912 |
| n_D^{20} | .. | .. | .. | .. | 1.5613 |
| α_D | .. | .. | .. | .. | inactive. |

On oxidation of a portion with potassium permanganate by the procedure of King and Murch (1925), an excellent yield of a *solid acid* (neutral equivalent, 152) crystallizing in needles from hot water, and melting at 183–184° (uncorr.), was obtained. The melting point was not depressed by mixing with an authentic specimen of *anisic acid* (neutral equivalent, 152 (calculated)).

A further portion of the material was oxidized by the method of Shoesmith (1923) and a pale yellow liquid of aubépin odour resulted. It yielded a *p*-nitrophenylhydrazone m.p. 161.5° (uncorr.) undepressed by admixture with *p*-anisaldehyde *p*-nitrophenylhydrazone.

It is therefore concluded that the compound is *anethole*.

ACKNOWLEDGEMENTS.

Thanks are due to the Director, Mr. A. R. Penfold, for permission to publish this note, and to Mr. R. J. Wailes for assistance with the distillation of the leaf.

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The Museum of Technology and
 Applied Science,
 Sydney.

NITROGEN IN OIL SHALE AND SHALE OIL.

VIII. THE DETECTION OF TAR BASES.

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INTRODUCTION.

In connection with other aspects of this work it became necessary to develop an unambiguous test for the detection of tar bases in crude shale oil and its products.

The tar bases present in shale oil are principally pyridine homologues, though weakly basic pyrrole homologues are also present (Mapstone, 1948). Crude shale oil also contains a large proportion of non-basic nitrogenous compounds of unknown composition (Mapstone, 1949), but these were not of importance in the work described here. Tests carried out on the oil could indicate the presence of either pyridine homologues or of pyrroles, while tests on an acid extract of the oil would be mainly indicative of the pyridine bases because of the very low acid solubility of the pyrroles.

With strongly coloured samples, it was necessary to extract the bases with acid before applying the tests. A number of different tests were therefore examined for sensitivity for the detection of tar bases in solution in the lighter oils and in solution in dilute sulphuric acid as they were extracted from the darker coloured oils.

SAMPLES TESTED.

The tar bases present in the acid sludge from the treatment of cracked shale gasoline were considered to be sufficiently representative of those initially present in the gasoline to be used for this work. They were therefore isolated as described previously (Mapstone, 1947) and purified by distillation. They contained 8.69% of nitrogen by weight, and the bases present would be almost entirely pyridine homologues.

Since preliminary work indicated the probable presence of approximately 5 p.p.m. of tar bases in refined shale gasoline, another suitable tar base-free hydrocarbon solvent was required for the determination of the sensitivity of the various reagents. The highly purified *n*-heptane-isoctane blend used for the determination of the octane rating of motor fuels was found to give a negative test with all except a few of the reagents used. In the cases where a positive result was obtained the reaction could be attributed to other factors. A 1% solution of the bases in the heptane-octane mixture (hereafter referred to as gasoline) was carefully prepared and the more dilute solutions prepared from it by dilution with further gasoline.

A solution of the purified bases in dilute sulphuric acid was prepared by dissolving 1.0 ml. of the bases in 250 ml. of 0.097 N sulphuric acid. Titration of portion of the solution showed that the excess acid was 0.0637 N, giving an 0.0333 N solution of the bases. This solution was diluted with further portions of the 0.0970 N acid to give the more dilute solutions required.

The light recycle oil (boiling range 5% at 360° F., 95% at 520° F) from the thermal cracking of crude shale oil is dark brown in colour, and it was therefore

necessary to extract the bases for detection. From the method of extraction and the boiling range the bases would be principally pyridine homologues together with any quinoline homologues that may be present. Fifty millilitres of the oil were washed with 200 ml. of 0.1061 N sulphuric acid. Titration of portion of the solution thus obtained showed that the excess acid was 0.0362 N, giving an 0.0699 N solution of the bases. This was diluted with further portion of the 0.1 N acid to give the more dilute solutions required.

With crude shale oil it was even more necessary than with the light recycle oil to extract the bases before detection. In the manner described for the light oil a 0.042 N solution of the bases from the crude shale oil was obtained in 0.1 N sulphuric acid.

Unless otherwise mentioned the tests on the hydrocarbon samples were carried out by adding two drops of the reagent to 5 ml. of the sample, and the tests on the acid extracts by adding four drops of the reagent to 1 ml. of the sample.

REAGENTS.

In deciding which reagents were to be tested, those which reacted with pyridine or quinoline or their homologues to give precipitates or developed colours were chosen. Since many alkaloids contain pyridine nuclei several "alkaloid" reagents were included. However, those alkaloid reagents which are based on concentrated sulphuric acid (e.g. Froehde's, Mandelin's and Erdmann's reagents) were not examined because of the action of the acid on the olefines in the gasoline samples, and with the samples dissolved in dilute acid, the dilution of the reagent would render them ineffective.

From the nature of their reaction with the tar bases the reagents were somewhat arbitrarily subdivided into seven classes which are discussed in turn.

(1) *Metal salts which precipitate the metal hydroxide.*

Pyridine and quinoline and their homologues are tertiary amines and their aqueous solutions can be sufficiently alkaline to precipitate the hydroxides from the solutions of the salts of various metals (Perkin, 1935). The sensitivity of the tests with such reagents would therefore depend principally on the solubility of the hydroxide of the metal, and the ease with which it could be seen when precipitated. The reagents were prepared by adding dilute ammonia dropwise to the aqueous solution of the metal salt until a slight permanent precipitate was formed. The reagent solution was used after filtration.

Five per cent. solutions of ferric chloride, cobalt nitrate, nickel nitrate, cupric nitrate and zinc chloride and a saturated solution of potassium alum were prepared in this manner. Another mixed reagent was prepared by the addition of 3 ml. of 1% ammonium aurine tricarboxylate solution to approximately 80 ml. of the saturated alum solution. A slight red precipitate was formed and removed by filtration. It was thought that the dye would be adsorbed on any aluminium hydroxide precipitate and render it more visible and thus possibly increase the sensitivity of the alum reagent.

On carrying out the test on samples with higher tar base concentrations a precipitate was thrown down but, with the limiting concentrations a film was formed at the gasoline-reagent interface. If an excess of reagent was used (e.g. 2 ml. per 5 ml. sample) the cobalt and aluminium reagents gave positive results even in the absence of tar bases. It was therefore necessary to adhere strictly to the test conditions in order to obtain reproducible results. The sensitivities of these reagents are presented in Table 1.

TABLE 1.
Sensitivities of Reagents.
Metal Salts which Precipitate the Metal Hydroxides.

| Reagent. | Colour of Precipitate. | Sensitivity. ¹ |
|--|------------------------|---------------------------|
| Ferric chloride | Red to yellow. | 0.0001%. |
| Cobalt nitrate | Pink. | Beyond 0.00005%. |
| Nickel nitrate | Green. | 0.0001%. |
| Cupric nitrate | Green-blue. | Beyond 0.00005%. |
| Zinc chloride | White. | Beyond 0.00005%. |
| Potassium alum | White. | 0.001%. |
| Alum plus ammonium aurine tricarboxylate | Reddish. | 0.001%. |

¹ Sensitivity is quoted as the least percentage of tar bases (8.7% N) by volume which gave a positive test.

Because the reaction between these reagents and the tar bases involves the precipitation of the acid soluble hydroxides of the metals, they were applicable to the detection of only the free bases and could not be applied to the acid extracts.

(2) *Acids which precipitate insoluble salts of the bases.*

This group of reagents includes many which have been used for the separation, isolation and identification of tar bases, and several "alkaloid" reagents. Because of their varied nature they are discussed separately. The sensitivities of the reagents are presented in Table 2.

TABLE 2.
Sensitivities of Reagents.
Acids which Precipitate Insoluble Salts of the Bases.

| Source of Bases. | Gasoline. | | Light Oil. | Crude Oil. |
|----------------------------------|--------------------------------------|--|--|--|
| Base dissolved in acid .. | Gasoline | 0.1 N H ₂ SO ₄ . | 0.1 N H ₂ SO ₄ . | 0.1 N H ₂ SO ₄ . |
| Chlorplatinic | 0.1% | Nil | Nil | 0.0001 N |
| Chlorauric | 0.05% | Nil | 0.00007 N | 0.00003 N |
| HCl in ether | 0.00005% | — | — | — |
| HCl (concentrated) | 0.005% | — | — | — |
| Picric | 0.001% | Nil | 0.02 N | 0.0012 N |
| Styphnic | 0.1% | Nil | 0.015 N | 0.0002 N |
| Trinitro- <i>m</i> -cresol | 0.05% | Nil | 0.015 N | 0.0002 N |
| Oxalic | 0.01% | — | — | — |
| Tannic | 0.2% | Nil | 0.03 N | 0.003 N |
| Phosphomolybdic | 0.0005% | Nil | Nil | 0.0002 N |
| Phosphotungstic | 0.05% | 0.003 N | 0.00007 N | 0.0002 N |
| Silicotungstic | 0.005% p.p.pt. 0.00005% colour | Nil | Nil | 0.002 N |

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(a) *Chlorplatinic Acid.* This reagent precipitates the sparingly soluble platinichlorides of the bases and has been used extensively for this purpose. It is of interest that the earliest recorded isolation and separation of the tar

bases from shale oil involved the precipitation of the bases as their platinum-chlorides which were separated by fractional crystallization (Williams, 1854, 1855). The reagent was prepared by dissolving 0.0942 gm. of platinum in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. of hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(b) *Chlorauric Acid*. This reagent is sometimes used to give sparingly soluble amine salts for the separation or identification of tar bases. It was prepared by dissolving 0.1998 gm. of pure gold in aqua regia, evaporating the solution to dryness on a water bath, dissolving in 2 ml. hydrochloric acid and making up to 20 ml. with distilled water. A positive test was indicated by the formation of a yellow-brown precipitate.

(c) *Hydrogen Chloride in Ether*. Since the hydrochlorides of the tar bases are insoluble in hydrocarbon solvents, the addition of hydrochloric acid should precipitate the chlorides, and as the precipitate would be soluble in water the sensitivity of the test should be increased by the use of an ethereal solution of hydrogen chloride. The reagent was prepared by saturating redistilled ether with hydrogen chloride gas. A positive test was indicated by a yellowish or white cloudiness in the sample. An excess of reagent gave a positive test in the absence of tar bases. This test was suitable for hydrocarbon samples only.

(d) *Hydrochloric Acid (Concentrated)*. This test was based on the considerations outlined in (c) above, but since it was an aqueous reagent it was not expected to be quite as sensitive. However, the reagent is always readily available and was therefore included for comparison. A positive result was indicated by a white cloudiness in the sample.

(e) *Picric Acid*. This reagent is frequently used for the isolation, separation and identification of basic organic compounds. The reagent was used in the form of the saturated aqueous solution. A positive result was indicated by the formation of a yellow precipitate or a yellow film at the gasoline-reagent interface.

(f) *Styphnic Acid*. This reagent is frequently used instead of picric acid for the same purposes and gives similar results which are no doubt due to the similarity of structure (styphnic acid is 3-hydroxy picric acid). The test was carried out as with picric acid and gave similar results.

(g) *Trinitro m-cresol*. This reagent (3-methyl picric acid) was included for comparison. The test was carried out as with picric acid and gave similar results.

(h) *Oxalic Acid*. The oxalates of pyridine homologues have sometimes been used for their separation and identification. The reagent was used as a saturated aqueous solution. A positive result was indicated by a white precipitate or film.

(i) *Tannic Acid*. This reagent is commonly employed as an "alkaloid" reagent, and was therefore included in this series of tests. This reagent was used as a 10% aqueous solution. The formation of a brown precipitate indicated a positive result.

(j) *Phosphomolybdic Acid*. This "alkaloid" reagent was prepared by the method of Hawke and Bergeim (1937). A positive result was indicated by the formation of a precipitate which was brown in higher concentrations and white in the lower concentrations. An excess of reagent gave a white precipitate even in the absences of the bases.

(k) *Phosphotungstic Acid*. This "alkaloid" reagent was prepared by the method of Hawke and Bergeim (1937). The test was carried out by adding two drops of the reagent to 5 ml. of the sample. A positive result was indicated by

the formation of a precipitate the colour of which increased from orange-yellow to white with decreasing tar base concentration.

(l) *Silicotungstic Acid*. This "alkaloid" reagent was prepared by dissolving 2 gm. of sodium tungstate in 10 ml. of hot water, adding 5 ml. of syrupy sodium silicate solution (s.g. 1.7), acidifying with 2 N nitric acid, diluting with 100 ml. of water, boiling and filtering. The clear filtrate was then acidified with 5 ml. of concentrated nitric acid. The tests were carried out using twice the usual proportion of the reagent. A positive test was indicated by the formation of a light brown precipitate or, in greater dilution, a pink colour in the gasoline sample.

(3) *Alkali salts which precipitate a salt of the base.*

(a) *Potassium Ferrocyanide*. This reagent is used for the detection of pyridine (Perkin, 1935) because of the low solubility of pyridine ferrocyanide. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a white precipitate with the lower boiling bases to deep brown precipitate with the higher boiling bases.

(b) *Potassium Dichromate*. This reagent is commonly used for the detection of quinoline (Perkin, 1935) because of the sparing solubility of quinoline dichromate. The reagent was used in the form of a saturated aqueous solution. A positive result was indicated by the formation of a yellow-orange to dark brown precipitate, the colour increasing with boiling point of the bases.

(c) *Potassium Triiodide*. This "alkaloid" reagent was prepared by dissolving 2 gm. of iodine and 4 gm. of potassium iodide in 100 ml. of water. A positive result was indicated by the formation of a brown precipitate.

The results of these tests are presented in Table 3.

TABLE 3.
Sensitivities of Reagents.

(a) Salts which precipitate a salt of the Base.

(b) Reagents which precipitate a double salt of the Base.

(c) Miscellaneous.

| Source of Bases. | Gasoline. | | Light Oil. | Crude Oil. |
|---------------------------|-----------|--|--|--|
| | Gasoline. | 0.1 N H ₂ SO ₄ . | 0.1 N H ₂ SO ₄ . | 0.1 N H ₂ SO ₄ . |
| Bases dissolved in | | | | |
| Reagent: | | | | |
| Potassium ferrocyanide .. | 0.5% | Nil | 0.03 N | 0.005 N |
| Potassium dichromate .. | 0.01% | Nil | 0.03 N | 0.004 N |
| Potassium triiodide .. | 0.05% | 0.001 N | 0.00001 N | 0.0001 N |
| Mercuric chloride .. | 0.05% | Nil | 0.03 N | 0.0002 N |
| Mayer's reagent .. | 0.0005% | 0.003 N | 0.0007 N | 0.0008 N |
| Dragendorff's reagent .. | 0.00005% | 0.0002 N | 0.00001 N | 0.0002 N |
| Sodium hydroxide .. | — | 0.015 N | 0.0035 N | 0.0002 N |
| Nessler's reagent .. | 0.001% | 0.003 N | 0.00002 N | 0.000002 N |

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

(4) *Reagents which give an insoluble double salt of the bases.*

The reagents discussed in this section could be classified in the previous section as the distinction is one of degree rather than type. The results are therefore presented with them in Table 3.

(a) *Mercuric Chloride*. With this reagent pyridine and quinoline and their homologues form complex mercurichlorides, usually of the form (BHCl)₂HgCl₂

but frequently the precipitated compound is more complex, e.g. 2·5 dimethyl pyridine gives the compound $C_7H_9N.HCl.6HgCl_2$ (Garrett and Smythe, 1902). The reagent was used in the form of a saturated aqueous solution. The formation of a precipitate indicated a positive result. With the lower boiling bases the precipitate was white, but it was more orange-brown with the crude oil bases.

(b) *Potassium Mercuric Iodide (Mayer's Reagent)*. This "alkaloid" reagent was prepared by dissolving 2·7 gm. of mercuric chloride and 10·0 gm. of potassium iodide in 190 ml. of water. A positive test was indicated by the formation of a precipitate, the colour of which was usually brown but, when near the limiting concentration of bases, was sometimes light brown, cream or even white.

(c) *Potassium Bismuth Iodide (Dragendorff's or Thresh's Reagent)*. This "alkaloid" reagent was prepared by the method outlined by Perkin (1935). A positive test was indicated by the formation of a red-orange precipitate, though the colour sometimes varied to red or brown.

(5) *Reagents which open the pyridine ring.*

The reagents discussed in this section cause the opening of the pyridine ring to give glutaconic aldehyde which forms brightly coloured Schiff's bases with primary aromatic amines.

(a) *Thionyl Chloride*. Pyridine can be converted into 4-pyridyl pyridinium chloride on heating with thionyl chloride and on treatment with alkali, this gives glutaconic aldehyde and 4-aminopyridine. Feigl and Anger (1939) developed a test which they reported to be sensitive to five γ of pyridine with a concentration limit of 1 : 10,000 by condensing the glutaconic aldehyde with α -naphthylamine. All attempts to apply this test even to the pure shale tar bases or to pure pyridine yielded negative results.

(b) *Cyanogen Halides*. Cyanogen halides react with pyridine to give the unstable *N*-cyano-pyridinium halide which is readily hydrolysed to glutaconic aldehyde. This reaction has been applied to the colorimetric determination of traces of cyanides (Epstein, 1947) as well as pyridine (Barta, 1935) and the detection of alkaloids containing a pyridine ring (Shmuk, 1940, 1942). In this work the three cyanogen halides were tested and the product reacted with a saturated aqueous solution of aniline or a 1% alcoholic solution of *p*-nitro-aniline, anthranilic acid, or α - or β -naphthylamine. The mixture was acidified and the colour change noted. The cyanogen chloride solution was prepared by adding 5 ml. of a 1% chloramine T solution to 2 ml. of a 1 N potassium cyanide solution. The cyanogen bromide and iodide solutions were prepared by adding bromine water or the potassium triiodide solution respectively to a 1 N potassium cyanide solution until there was a slight excess of the free halogen; this was removed by the addition of a few drops of the cyanide solution. The test was carried out by shaking 5 ml. of the sample with 1 ml. of the cyanogen halide solution followed by the addition of 1 ml. of the amine solution. After the colour had been noted concentrated hydrochloric acid was added dropwise until no further change occurred. With the cyanogen chloride and bromide the tests were satisfactory, but iodine was precipitated on acidification of the tests with cyanogen iodide. The results are presented in Table 4.

(6) *Salts which give co-ordination compounds with pyridine.*

Pyridine is noted for the large number of co-ordination complexes which it forms with metallic salts, but in order that such compounds may be used for the detection of pyridine or its homologues, they should either be insoluble in or extractable from the reaction medium, and should be preferably strongly

TABLE 4.
Sensitivities of Reagents.
Cyanogen Halides and Aromatic Amines.

| Source of Bases. | Gasoline. | | Light Oil. | Crude Oil. |
|----------------------------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|
| Bases dissolved in | Gasoline | 0.1 N H ₂ SO ₄ | 0.1 N H ₂ SO ₄ | 0.1 N H ₂ SO ₄ |
| A. Cyanogen chloride with— | | | | |
| Aniline : | | | | |
| Test | y. to r.br. | wh. to c. | wh. to c. | y. to c. |
| Sensitivity | 0.75% | 0.003 N | 0.000001 N | 0.000004 N |
| p-Nitro-aniline : | | | | |
| Test | y. to or. | y. to c. | y. to c. | y. to c. |
| Sensitivity | 0.75% | 0.015 N | 0.000003 N | 0.00001 N |
| Anthranilic acid : | | | | |
| Test | y. to r.br. | wh. to c. | wh. to c. | y. to c. |
| Sensitivity | 0.75% | 0.002 N | 0.000001 N | 0.000002 N |
| α-Naphthylamine : | | | | |
| Test | lt.y. to r.br. | p. to c. | y. to c. | y. to c. |
| Sensitivity | 0.75% | 0.003 N | 0.000001 N | 0.000002 N |
| β-Naphthylamine : | | | | |
| Test | y.br. to br. | m. to c. | w. to y. | br. to lt.br. |
| Sensitivity | 0.00005% | 0.016 N | 0.006 N | 0.00002 N |
| B. Cyanogen bromide with— | | | | |
| Aniline : | | | | |
| Test | y. to r.br. | Nil | cr. to c. | cr. to c. |
| Sensitivity | 0.75% | — | 0.00003 N | 0.00004 N |
| p-Nitro-aniline : | | | | |
| Test | y. to r.br. | y. to c. | y. to c. | cr. to c. |
| Sensitivity | 0.25% | 0.003 N | 0.00003 N | 0.00002 N |
| Anthranilic acid : | | | | |
| Test | y. to r.br. | y. to r.br. | y. to c. | cr. to c. |
| Sensitivity | 0.75% | 0.016 N | 0.000015 N | 0.00003 N |
| α-Naphthylamine : | | | | |
| Test | br. to r.br. | cr. to c. | cr. to c. | cr. to c. |
| Sensitivity | 0.75% | 0.0013 N | 0.00003 N | 0.00004 N |
| β-Naphthylamine : | | | | |
| Test | br. to lt.br. | y.br. to br. | y. to lt.y. | br. to lt.br. |
| Sensitivity | 0.00005% | 0.016 N | 0.0003 N | 0.00004 N |

The sensitivities are quoted as percentages of tar bases (10% N) in the gasoline sample, and as normalities in the diluted acid solutions.

Key :

| | | |
|------------------|--------------|---------------|
| br. = brown. | m. = milky. | y. = yellow. |
| c. = colourless. | p. = pink. | or. = orange. |
| cl. = clear. | r. = red. | lt. = light. |
| cr. = creamy. | wh. = white. | |

coloured. A preliminary survey suggested that the acetates, thiocyanates and cyanates of cobalt, nickel and copper were worth investigation as they were coloured and could be extracted from the aqueous solution by chloroform (Morton, 1946). The results are presented in Table 5.

(a-c) *Acetates*. Since the acetates of cobalt, nickel and copper are soluble in water, and the complexes are soluble in chloroform as well as water, they could be extracted satisfactorily from the acid solutions of the bases once formed. A preliminary examination indicated that the complex was stable and could be extracted from the aqueous solution only if the pH was greater than 4. The acetate reagent was therefore prepared to act as a buffer solution as well as to provide acetate ions by dissolving 15 gm. of sodium acetate crystals and 20 ml. of glacial acetic acid in sufficient water to give 100 ml. of solution. The test was

TABLE 5.
Sensitivities of Reagents.
Co-ordination Complexes with Salts.

| Source of Bases. | Gasoline. | | Light Oil. | Crude Oil. |
|--------------------------------------|-----------|--------------------------------------|--------------------------------------|--------------------------------------|
| Bases dissolved in Salt : | Gasoline | 0.1 N H ₂ SO ₄ | 0.1 N H ₂ SO ₄ | 0.1 N H ₂ SO ₄ |
| Cupric acetate | — | 0.00025 N | 0.00007 N | 0.00025 N |
| Cobalt acetate | — | 0.00025 N | 0.00015 N | 0.00005 N |
| Nickel acetate | — | 0.0005 N | 0.0003 N | 0.00025 N |
| Cupric thiocyanate | 1.0% | 0.003 N | 0.002 N | 0.002 N |
| Cobalt thiocyanate | 0.1% | 0.007 N | 0.0008 N | 0.004 N |
| Nickel thiocyanate | 0.1% | 0.003 N | 0.0009 N | 0.004 N |
| Cupric carbamate (?) | — | 0.001 N | 0.002 N | 0.0003 N |
| Cobalt carbamate (?) | — | 0.0005 N | 0.0001 N | 0.0001 N |
| Nickel carbamate (?) | — | 0.001 N | 0.003 N | 0.0005 N |

The sensitivities are quoted as percentage of tar bases (8.7% N) by volume in the gasoline solution, and as normalities in the dilute sulphuric acid solutions.

carried out by adding 1 ml. of this acetate reagent and 0.5 ml. of a 5% solution of the cobalt, nickel or cupric nitrate, and 1 ml. of chloroform, to 5 ml. of the solution of the tar bases in dilute sulphuric acid. The mixture was shaken and allowed to stand when the development of an amber colour in the chloroform layer indicated a positive test.

With pyridine the cupric acetate complex was green, but with the shale tar bases it was amber. This was first thought to be due to some impurity in the reagent but was later found to be due to the difference in the bases themselves. For comparison the tests were carried out using some pyridine which had been carefully freed from all homologues by refluxing with permanganate, and different boiling fraction of mixtures of pyridine homologues. The lower boiling homologues were obtained by fractionating denaturant grade pyridine (from coal tar) through a 12 pear column and the higher boiling fractions were obtained in previous work (Mapstone, 1947) by the careful fractionation of the shale tar bases through a 36-inch Fenske column at high reflux.

The results obtained are presented in Table 6, and indicate that the boiling range of the bases influence the colour of the complex formed. The tests were carried out on solutions containing two drops of the bases in 5 ml. of 0.1 N sulphuric acid.

Although pyridine gives complexes with salts of substituted acetic acids and its homologues (Morton, 1946 ; Reitzenstein, 1902, 1940), they were not included as it was felt that they would have little advantage, if any, over the acetates.

(d) *Cupric Thiocyanate.* The formation of a precipitate, $\text{Cu}(\text{CNS})_2 \cdot 2\text{C}_6\text{H}_5\text{N}$, which is soluble in chloroform to give an emerald green solution, is reported to be sensitive to 0.05% of pyridine (Morton, 1946 ; Spacu, 1922, 1923). In this work the test was carried out by adding two drops of a solution of 5 gm. of potassium thiocyanate in 10 ml. of water and two drops of a 0.5% solution of cupric nitrate to 5 ml. of the sample. This gave a black to greenish black precipitate of cupric thiocyanate. With the acid solutions the complex was extracted by the addition of 2 ml. of chloroform. A positive result was indicated by a green colour in the chloroform. With the acid samples containing the tar bases from gasoline the chloroform coagulated the dark green cupric thiocyanate precipitate and gave a yellowish-white precipitate at the interface. With the gasoline solution of the bases the black precipitate of cupric thiocyanate interfered with the observation of any colour. In this case the precipitate was

TABLE 6.
Effect of Boiling Point of Bases on Colour of Acetate Complex.

| Base. | Colour of Complex in Chloroform. | | |
|--------------------------------|----------------------------------|-------------------------|-------------------------|
| | Cobalt. | Nickel. | Cupric. |
| Pure pyridine | Amber. | Yellow-green. | Green. |
| Coal tar bases to 117° C. .. | Light yellow. | Light yellow. | Green-lemon. |
| " " 117-133° C. .. | " | " | Light green. |
| " " 133-145° C. .. | " | " | Light yellow. |
| " " 145-155° C. .. | " | " | Lemon-green. |
| Shale tar bases 164-170° C. .. | Very pale bluish green. | Very pale bluish green. | Very pale bluish green. |
| " " 170-180° C. .. | Yellowish green. | Yellowish green. | Yellowish green. |
| " " 180-190° C. .. | Yellowish green. | Yellowish green. | Yellowish green. |
| " " 190-200° C. .. | Yellow. | Yellow. | Yellow. |
| " " 200-210° C. .. | Yellow. | Yellow. | Yellow. |
| " " 210-212° C. .. | Greenish amber. | Greenish amber. | Amber. |
| " " <i>ex</i> gasoline .. | Amber. | Amber. | Amber. |
| " " <i>ex</i> light oil .. | Amber. | Light amber. | Amber. |
| " " <i>ex</i> crude oil | Amber. | Light amber. | Amber. |

Remarks : The colour developed with the shale tar bases increased in intensity with increasing boiling point. The colours observed ranged through all the various shades mentioned but did not show quite as much difference as may appear to be indicated by the table.

filtered off and washed with 2-3 ml. of chloroform, the washings being collected separately. A positive test was indicated by the formation of a green colour in the chloroform washings.

(e) *Nickel Thiocyanate*. These tests were carried out as with the cupric salt using a 5% solution of nickel nitrate. With the solution of tar bases in gasoline a positive test was indicated by the formation of a green colour in the reagent and a white to green interfacial precipitate. Since the nickel thiocyanate was soluble in water the filtration step was not necessary. No precipitate was formed with the acid solutions of tar bases, but a positive test was indicated by the formation of an amber colour in the lower phase on shaking with chloroform.

(f) *Cobalt Thiocyanate*. These tests were carried out as with the cupric and nickel salts using a 5% solution of cobalt nitrate. As with the nickel salt, the cobalt thiocyanate did not precipitate and interfere with the observations of the test. With the tar bases in gasoline a positive result was indicated by the formation of a green precipitate. With the acid solutions a positive test was indicated by the formation of a greenish blue colour in the chloroform layer.

(g-i) *Cyanates (Carbamates)*. The formation of the dipyridine complex of cupric cyanate has been described for the detection of copper or cyanate, the complex being soluble in chloroform to give an azure blue solution (Morton, 1946 ; Werner, 1925 ; Vogel, 1945). The complex cobalt and nickel pyridine cyanates are also soluble in chloroform (Morton, 1946 ; Davis and Logan, 1928, 1934). Since potassium cyanate is not readily available commercially, it was prepared by two different methods for comparison ; the oxidation of fused potassium cyanide with litharge, and oxidation in solution with the calculated amount of potassium permanganate. In each case the freshly prepared solution gave the same results, and in each case also the solution decomposed on standing, so that no cyanate could be detected in the reagent solution after standing for a few hours even though the test applied was sensitive to one part of cyanate in 20,000 (Vogel, 1945), although this solution still gave

colour reactions with the tar bases, of comparable sensitivity with the acetates and thiocyanates. Hydrolysis of the cyanate would give a carbamate and then a carbonate, but carbonates did not give the colour reactions. It is therefore suggested that the colour reactions observed are due to the formation of complex pyridine cupric carbamate and the corresponding cobalt and nickel salts.

The cyanate (or carbamate) reagent was prepared by adding a solution of 5.5 gm. (0.033 gm. mol) of potassium permanganate in 40 ml. of water containing 3.3 ml. (0.033 mol) of concentrated hydrochloric acid to a solution of 3.3 gm. (0.05 mol) of potassium cyanide, followed by suction filtration to remove the precipitated manganese dioxide. The object of adding the acid was to neutralize the potassium hydroxide formed during the oxidation, but it did not appear to stabilize the cyanate solution and could be omitted without effect. The test was applied to the acid solutions of the bases only, as significant results could not be obtained with the gasoline solution of the bases. The test was carried out by adding two drops of the cyanate solution and two drops of the metal nitrate solution (as for the thiocyanate tests) to 5 ml. of the sample. Dilute (5%) acetic acid was added dropwise until the precipitated (hydroxide and/or carbonate of the metal) dissolved and the complex then extracted by shaking with 2 ml. of chloroform. A positive result was indicated by the formation of a colour in the chloroform layer. With a cyanate solution that had been freshly prepared the colours obtained were: copper, light blue; cobalt, royal blue; nickel, pale green. If the cyanate solution had been prepared for more than half an hour the colours obtained were: copper, green to amber, depending on the boiling range of the bases; cobalt, amber to red; nickel, orange to brown. Because of the instability of the fresh reagent the sensitivity of the test with only the more stable hydrolysed solution was determined.

(7) *Miscellaneous tests.*

In this section are listed those tests that cannot be included in any of the previous categories. The results are presented in Table 3.

(a) *Sodium Hydroxide.* Addition of this reagent to an acid solution of the bases liberates the free bases. Although pyridine itself is completely miscible with water, the solubility of the homologues decreases rapidly with increasing molecular weight. The test therefore depends on the sparing solubility of the liberated mixture of the bases in water. The reagent was used as a 10% aqueous solution and a positive result was indicated by the formation of a white precipitate or white cloudiness.

(b) *Condensation with Sodium 1:2-naphthaquinone-4-sulphonate.* Feigl and Frehden (1934) observed that *N*-alkyl pyridinium compounds readily condense with 1:2-naphthaquinone-4-sulphonic acid to give coloured compounds. The test was carried out using methyl iodide and dimethyl sulphate as alternative alkylating agents and gave yellow to red colours with the bases. However, similar colours were obtained in the absence of the bases when the test was applied to the gasoline and sulphuric acid used to dissolve the bases. This may be due to the condensation of the sulphuric acid reagent with other reactive compounds (Erlich and Herter, 1904).

(c) *Nessler's Reagent.* This reagent is the most sensitive reagent known for the detection of ammonia and has recently been shown to be even more sensitive for the detection of aromatic secondary amines than for ammonia (Liebhafsky and Bronk, 1948). Nichols and Willits (1934) thoroughly investigated the reaction of the reagent with ammonia and concluded that the product was a colloidal suspension of the composition $\text{NH}_2\text{Hg}_2\text{I}_3$. Primary and secondary amines could therefore be expected to give the analogous products $\text{RNH}\cdot\text{Hg}_2\text{I}_3$.

and $\text{NR}_2\text{Hg}_2\text{I}_2$, respectively, and the tertiary amines may be expected to react as with Mayer's reagent. This reagent was prepared in the manner described by Perkin (1935). When tested with the heptane-octane mixture the reagent gave a slight yellow-green precipitate on standing for 10-15 seconds, in the absence of added tar bases. Because of this the sensitivity of the reagent for the detection of tar bases in gasoline solution was determined with solutions of the bases in a sample of the gasoline that had been washed with the reagent until no further precipitate was formed, and then water washed and filtered. The formation of a precipitate in the absence of added tar bases was probably due to the presence of aldehydes in the gasoline as it has been shown that Nessler's reagent can give a positive response to 1 p.p.m. of acetaldehyde in ether (van Deripe, Billheimer and Nitardy, 1936). With the solution of the bases in gasoline a positive test was indicated by the formation of a precipitate, the colour of which was usually greenish-yellow but, when near the limiting concentrations, was yellow to cream. With the acid solutions of the bases the reagent gave a white to cream precipitate.

SUMMARY.

Sixty-four different tests have been examined for their sensitivity for the detection of shale tar bases (essentially pyridine homologues). Thirty-nine of the tests are suitable for the detection of the lower boiling bases in solution in gasoline; 26 for the detection of the bases from the gasoline in solution in dilute acid; 33 for the detection of the bases from the light oil in solution in dilute acid; and 36 for the detection of the bases from the crude oil in solution in dilute acid.

ACKNOWLEDGEMENTS.

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NITROGEN IN OIL SHALE AND SHALE OIL.

IX. DENSITY-TEMPERATURE RELATIONSHIPS OF SHALE TAR BASES.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

Manuscript received, March 7, 1949. Read, April 6, 1949.

INTRODUCTION.

In working with the tar bases isolated from the gasoline obtained by the thermal cracking of crude shale oil, it was frequently found necessary to apply temperature corrections to density measurements. Since the standard correction tables for petroleum products were not applicable to the bases and no coefficient of expansion data were available, the work reported here was carried out to make up the deficiency.

BASES USED.

A quantity of tar bases were liberated by caustic soda from the hydrolysed acid sludge from the refining of the gasoline as described previously (Mapstone, 1947). Four and a half litres of the bases were distilled from a one-gallon iron pot through a twelve pear glass fractionating column. The distillate was collected in seventeen 250 ml. portions which were used for the subsequent work.

A quantity of the light recycle oil from the Dubbs cracking plant was extracted with hydrochloric acid. The bases were recovered as above and, after drying over solid caustic soda, were distilled. The distillate was used for the subsequent work.

DENSITY DETERMINATIONS.

The density of the bases was determined to four significant figures with a Westphal balance. The vessel containing the sample was well lagged so that the density of the bases could be determined over a range of temperatures. The bases were heated to 80–90° C. and poured into the sample vessel. When the rate of cooling had become steady the density was determined. By taking reasonable precautions it was possible to obtain results reproducible within the accuracy of the test (I.P. 59/45, 1948). Several other density determinations were carried out during the 1–2 hours required for the sample to cool to about 35° C. The sample was then chilled to about 5° C. and further density determinations were carried out on it as it warmed up. A minimum of six densities were determined on each sample at different temperatures.

The density-temperature relationships were determined for only ten of the eighteen samples as the specific gravities of the remaining samples were sufficiently close to others not to warrant their being checked.

When the observed densities were plotted against the temperature, a series of straight lines was obtained (Figure 1). Two fractions of the bases (Nos. 2 and 11) had the same density within experimental error, though there was a difference of 32° C. in their mean boiling points. This also indicated that the coefficient of expansion was a simple function of the density and not of the boiling point of the sample.

COEFFICIENT OF EXPANSION.

The coefficient of expansion of each of the samples of the bases was calculated from the slope of the density-temperature curves from Figure 1. It was immediately evident that the coefficient of expansion was much higher than the corresponding figure for petroleum products and that it varied appreciably with the density of the bases. The coefficient of expansion did not give a perfect correlation when plotted against the density of the sample at 20° C. (read from Figure 1) but the results (Figure 2) indicated that the relationship was most probably linear. The method of Hanson (1947) was applied to determine the most probable correlation. This was

$$\alpha = 0.02739 - 0.01964 D_{20}$$

where α = coefficient of expansion

D_{20} = density of bases at 20° C.

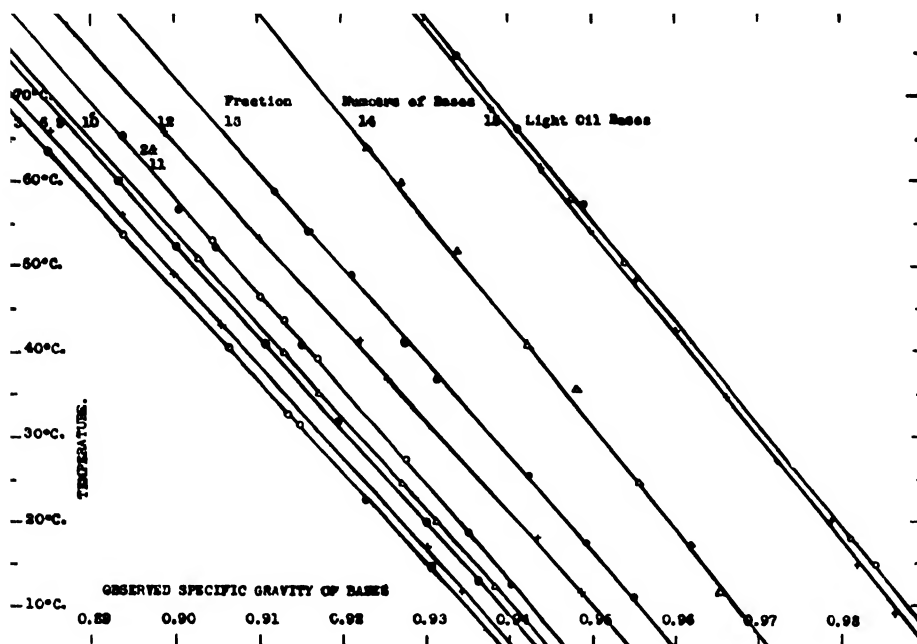


Fig. 1.—Variation of Specific Gravity of Tar Bases with Temperature.

Substituting this value of α in the usual density correction formula

$$D_t = D_{20} - \alpha(t - 20) \quad \dots \dots \dots (2)$$

where D_t = density at t° C.

gives

$$D_t = D_{20} - (0.02739 - 0.01964 D_{20})(t - 20) \quad \dots \dots (3)$$

as the overall relationship between the density and temperature for the shale tar bases. This relationship is presented in simple nomographic form in Figure 3. By means of this nomograph the density of any sample of the bases may be rapidly and simply corrected to 20° C. and, if required, calculated to any other temperature. The use of the nomograph is much simpler and more accurate than interpolation on Figure 1.

BOILING POINT-DENSITY RELATIONSHIPS.

Since the tar base fractions used to determine the density-temperature relationships were mixtures, they distilled over fairly wide temperature ranges.

For purposes of comparison, therefore, the volumetric average boiling point was calculated for each sample as the average of the temperatures at which 10%, 30%, 50%, 70% and 90% of the material had distilled under standard conditions (I.P. 28/42). The results are expressed graphically in Figure 4, which shows that, with increasing volumetric average boiling point of the bases the density first decreased and then increased.

Relatively few data are available for the density of different fractions of shale tar bases, and those that are generally apply to carefully treated fractions and cannot, therefore, be expected to be representative of the crude bases. However, Cane (1942) reported the densities of some narrow boiling fractions from shale tar bases which had not been otherwise treated and these show an increase in density with the boiling point.

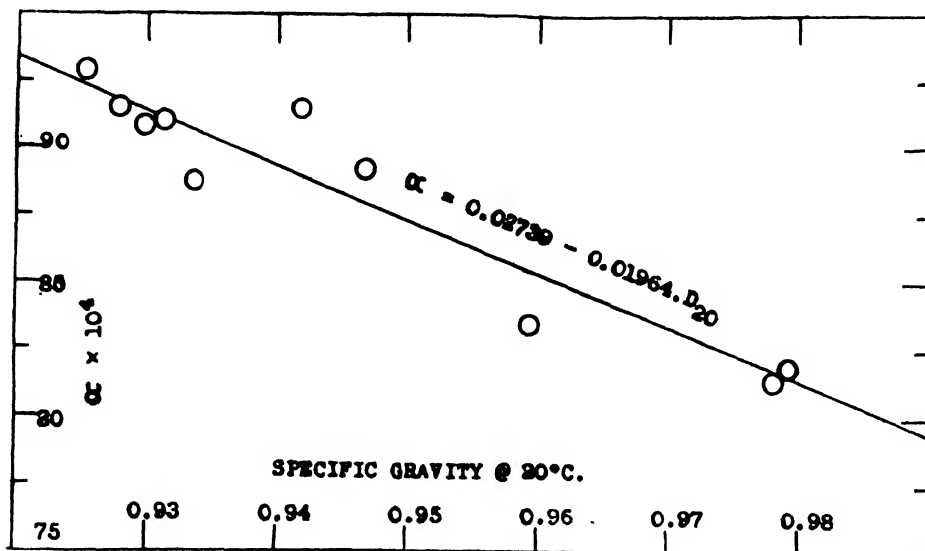


Fig. 2.—Correlation between Coefficient of Expansion and Specific Gravity of Shale Tar Bases.

The densities of alkyl pyridines, which appear to constitute the bulk of the bases, give a scatter relationship, as is to be expected, when they were plotted against the boiling points (Figure 4). By way of comparison with the unpurified bases, the data for pyridine homologues isolated from Fushun shale oil by Eguchi (1927, 1928) have been included in Figure 4. The densities recorded by Eguchi were corrected to 20° C. by means of Figure 3.

It is interesting to note that the density values for the crude tar bases lies within the spread of results for the purified bases isolated by Eguchi with the exception of the higher boiling fractions. However, the presence of a fair proportion of Eguchi's pyrindane or its homologues could readily explain the rapid increase in density with boiling point.

SUMMARY.

The variation of the specific gravity of shale tar bases with temperature has been determined and the coefficient of expansion has been correlated with the specific gravity at 20° C. The results are presented in the form of a nomograph. The specific gravity of the bases first decreases and then increases with the boiling point.

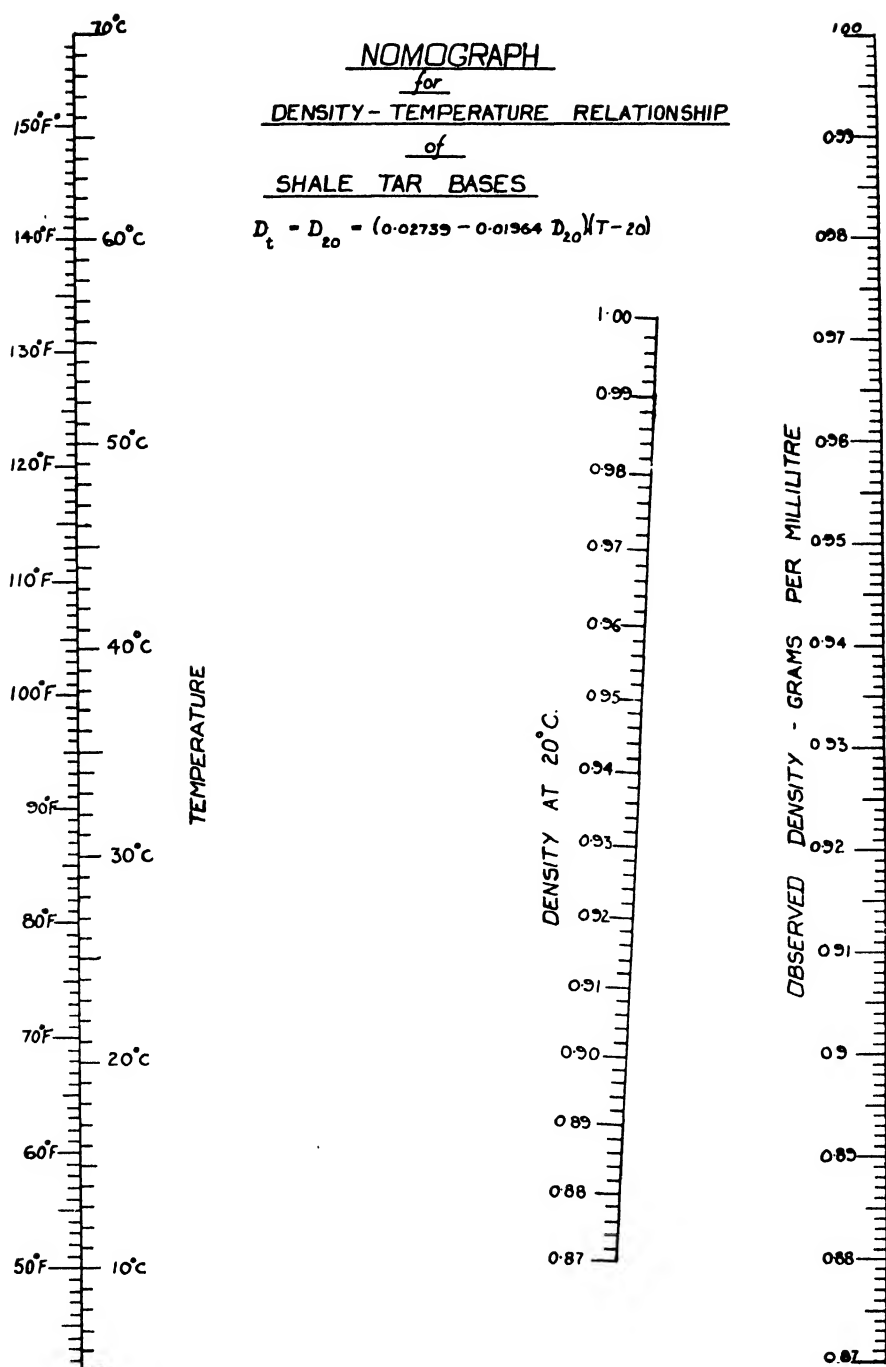


Fig. 3.

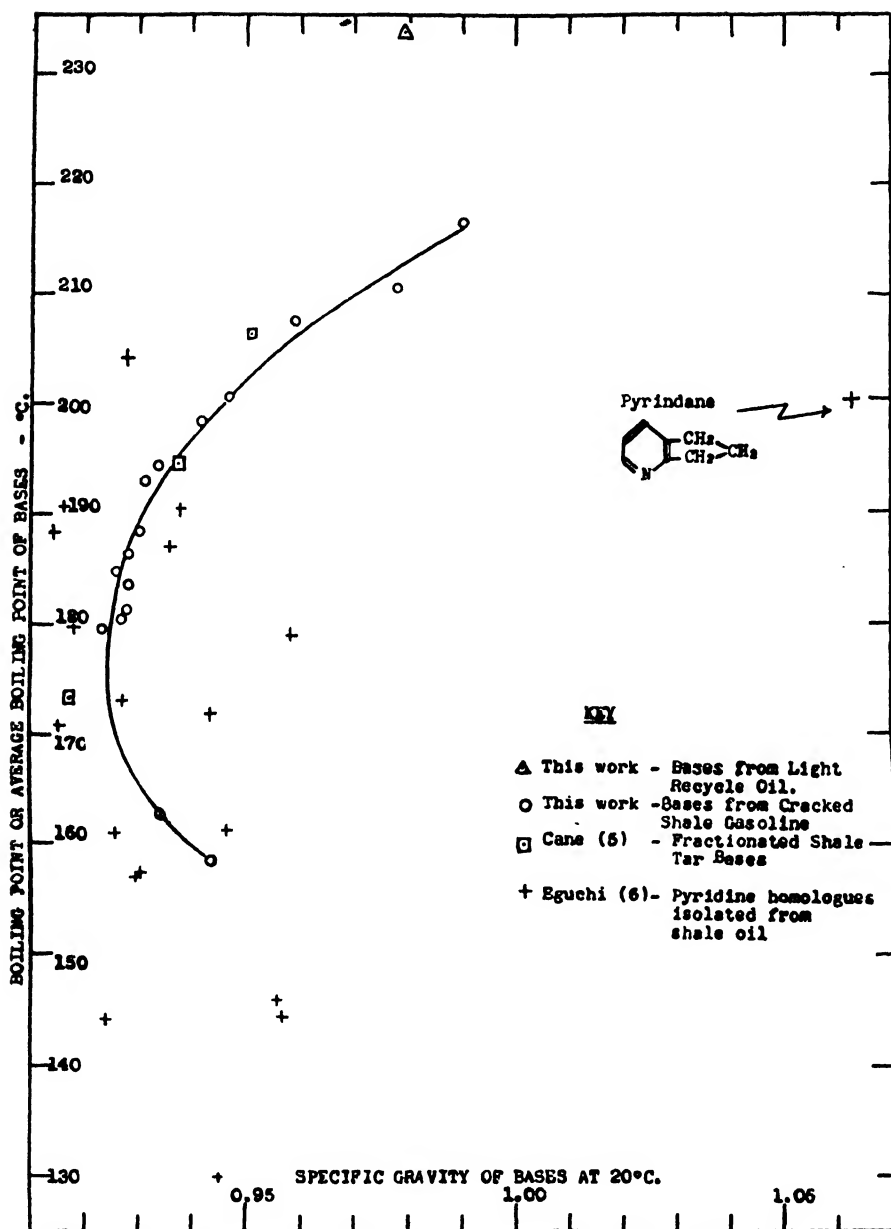


Fig. 4.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge with thanks the assistance of R. J. Dalton in carrying out the experimental work, and the permission granted by the management of National Oil Pty. Ltd. for the publication of this paper.

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OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1948.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, December 16, 1948. Read, April 6, 1949.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph. No correction was applied to the recorded times, either for personal effect, or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the *Nautical Almanac* for 1938 and the reduction completed by the method given there. The necessary data were taken from the *Nautical Almanac* for 1948, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

TABLE 1.

| Serial No. | N.Z.C. No. | Mag. | Date. | U.T. | Observer. |
|---------------|---------------|------|----------|------------|-----------|
| | | | | h m s | |
| 164 | 429 | 6.9 | Mar. 15 | 8 47 41.0 | R |
| 165 | 996 | 6.8 | Apr. 15 | 8 13 24.1 | W |
| 166 | 1424 | 6.8 | Apr. 18 | 10 25 56.3 | W |
| 167 | 1621 | 7.5 | May 17 | 7 34 40.5 | R |
| 168 | 1864 | 6.8 | May 19 | 12 18 28.3 | R |
| 169 | 1869 | 6.1 | May 19 | 13 46 32.9 | W |
| 170 | 1598 | 6.4 | June 13 | 9 51 11.9 | W |
| 171 | 2025 | 6.8 | July 14 | 9 22 31.8 | R |
| 172 | 2228 | 5.9 | Aug. 12 | 9 32 02.8 | W |
| 173 | 2398 | 6.1 | Aug. 13 | 14 44 55.2 | W |
| 174 | 1946 | 7.2 | Sept. 6 | 9 34 58.3 | R |
| 175 | — | 7.7 | Sept. 6 | 9 41 06.1 | R |
| 176 | 2069 | 7.3 | Sept. 7 | 10 21 41.7 | W |
| 177 | 2189 | 7.0 | Sept. 8 | 9 13 10.4 | R |
| 178 | 2479 | 5.3 | Sept. 10 | 11 25 02.6 | R |
| 179 | 2480 | 5.3 | Sept. 10 | 11 25 15.8 | R |
| 180 | 2482 | 6.7 | Sept. 10 | 11 46 10.4 | R |
| 181 | 2634 | 7.4 | Sept. 11 | 12 21 55.4 | W |
| 182 | 2650 | 4.7 | Sept. 11 | 14 36 51.7 | W |
| 183 | 2796 | 6.8 | Sept. 12 | 12 11 46.0 | W |
| 184 | 3175 | 4.8 | Sept. 15 | 11 08 35.0 | W |
| 185 | 3265 | 6.6 | Oct. 13 | 10 42 10.0 | R |
| 186 | 3106 | 5.4 | Nov. 8 | 13 40 17.2 | R |

Table 1 gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1948). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table 2 gives the results of the reductions

TABLE 2.

| Serial No. | Luna-tion. | p | q | p^2 | pq | q^2 | $\Delta\sigma$ | $p\Delta\sigma$ | $q\Delta\sigma$ | Coefficient of | |
|------------|------------|------|-----|-------|------|-------|----------------|-----------------|-----------------|----------------|----------------|
| | | | | | | | | | | $\Delta\alpha$ | $\Delta\delta$ |
| 164 | 312 | + 90 | +43 | 81 | +39 | 19 | -1.6 | -1.4 | -0.7 | + 9.7 | +0.73 |
| 165 | 313 | + 99 | -12 | 99 | -12 | 1 | -0.3 | -0.3 | 0.0 | +13.1 | -0.11 |
| 166 | 313 | + 99 | -15 | 98 | -15 | 2 | -0.2 | -0.2 | 0.0 | +12.4 | -0.47 |
| 167 | 314 | + 80 | +60 | 64 | +48 | 36 | -2.3 | -1.8 | -1.4 | +14.3 | +0.21 |
| 168 | 314 | + 89 | +46 | 79 | +41 | 21 | -1.5 | -1.3 | -0.7 | +15.0 | 0.00 |
| 169 | 314 | + 98 | +18 | 97 | +18 | 3 | -1.5 | -1.5 | -0.3 | +14.4 | -0.29 |
| 170 | 315 | + 87 | -50 | 75 | -43 | 25 | -0.7 | -0.6 | +0.4 | + 8.5 | -0.82 |
| 171 | 316 | + 92 | +40 | 84 | +37 | 16 | -1.7 | -1.6 | -0.7 | +14.7 | -0.02 |
| 172 | 317 | + 94 | -34 | 88 | -32 | 12 | -0.1 | -0.1 | 0.0 | +11.0 | -0.62 |
| 173 | 317 | + 27 | +96 | 7 | +26 | 93 | -1.0 | -0.3 | -1.0 | + 6.3 | +0.89 |
| 174 | 318 | +100 | + 4 | 100 | + 4 | 0 | -0.6 | -0.6 | 0.0 | +13.5 | -0.41 |
| 175 | 318 | + 99 | +17 | 97 | +17 | 3 | -1.3 | -1.3 | -0.2 | +14.1 | -0.29 |
| 176 | 318 | + 84 | -55 | 70 | -46 | 30 | +1.4 | +1.2 | -0.8 | + 8.0 | -0.84 |
| 177 | 318 | + 81 | +58 | 66 | +47 | 34 | -1.7 | -1.4 | -1.0 | +13.6 | +0.27 |
| 178 | 318 | + 74 | -68 | 54 | -50 | 46 | +0.2 | +0.1 | -0.1 | + 8.5 | -0.77 |
| 179 | 318 | + 73 | -68 | 53 | -50 | 47 | +0.6 | +0.4 | -0.4 | + 8.4 | -0.78 |
| 180 | 318 | + 90 | -44 | 81 | -40 | 19 | 0.0 | 0.0 | 0.0 | +11.1 | -0.56 |
| 181 | 318 | + 98 | -19 | 96 | -19 | 4 | -1.0 | -1.0 | +0.2 | +13.0 | -0.22 |
| 182 | 318 | + 34 | +94 | 12 | +22 | 88 | -1.4 | -0.5 | -1.3 | + 4.7 | +0.93 |
| 183 | 318 | + 99 | -15 | 98 | -15 | 2 | -1.0 | -1.0 | +0.2 | +13.3 | -0.06 |
| 184 | 318 | + 99 | -16 | 97 | -16 | 3 | -0.1 | -0.1 | 0.0 | +13.9 | +0.19 |
| 185 | 319 | + 98 | -20 | 96 | -20 | 4 | -1.7 | -1.7 | +0.3 | +14.1 | +0.19 |
| 186 | 320 | +100 | + 8 | 99 | + 8 | 1 | -1.0 | -1.0 | -0.1 | +12.9 | +0.39 |

which were carried out in duplicate. The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950.0 (Robertson, 1940), as recorded in the *Nautical Almanac*.

The star involved in occultation 175 was not included in the *Nautical Almanac* list; it is G.C. 18326 (apparent place R.A. 13^h 30^m 44^s.10, Dec. -8° 10' 14".0).

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PROCESSES IN DIELECTRICS CONTAINING FREE CHARGES.

THE ENTROPY OF ELECTROSTATIC SYSTEMS.

By B. BREYER, Ph.D. M.D. F.A.C.I.
and F. GUTMANN, Ph.D. M.I.R.E. F.Inst.P.

Manuscript received, November 11, 1948. Read, April 6, 1949.

I. INTRODUCTION.

The dielectric behaviour of a space can be described in terms of its permittivity and conductivity, which then can be combined in a complex dielectric "constant" ϵ . The permittivity, given by the real part of ϵ , is a measure of the free electrostatic energy, which is available for doing reversible work, and is stored in the dielectric. The conductivity, which can also be expressed in terms of the dielectric loss angle $\tan \delta$, to which it gives rise, is a measure of the degree of how far the energetic state of the dielectric under applied electric stress is a state of labile equilibrium, i.e. how much energy must be expended in order to maintain that equilibrium state.

In an ideal vacuum condenser, all the energy stored in the field can be recovered without loss: it is free electrostatic energy, capable of doing reversible work. If the dielectric is filled with a polarizable substance, but still imagined loss-free, the energy stored will be greater depending on the permittivity of the substance, but it will still remain free electrostatic energy which can be reversibly recovered without loss.

Dielectric losses can arise from two fundamentally different causes: firstly, due to imperfections and losses in the polarization process, i.e. by the necessity for the expenditure of energy for the alignment and dealignment of the atoms and/or molecules, and secondly, due to the presence of free charges in the dielectric. A very considerable amount of study has been devoted to polarization losses. It is the purport of the present paper to investigate theoretically the influence of a space-charge in a dielectric on its dielectric behaviour.

II. ANALYSIS.

An ideal vacuum condenser, of capacity C_{vac} , one plate of which is charged to a potential V with reference to the other plate, has stored free electrostatic energy W_f (capable of doing reversible work), and is given by

$$W_f = \frac{1}{2} V^2 C_{\text{vac}} \quad (1)$$

The sign of W_f depends on the point of view: following usual thermodynamic convention, it will be taken as negative if work equal to W_f can be done reversibly by the system.

If now the vacuum is filled with any material medium, V being maintained at its previous value, the quantity of free energy stored will be altered. It is therefore possible to define the electrostatic capacity of a system from equation (1):

$$C = 2W_f/V^2 \quad (2)$$

The permittivity of the dielectric, or the real part of ϵ , will then be given by

$$\epsilon' = C/C_{\text{vac}} = D \quad (3)$$

Considering now a plane parallel condenser of unit area, whose plates are separated by a distance a and connected by resistance-less leads to a source of $EMF = V$: when the dielectric between the plates is a loss-free medium of permittivity D , the work done in charging the plates is W_0 . Because the dielectric is loss-free, all the energy W_0 then is free energy stored in the dielectric.

If now a space distribution of charges of local density $\rho = f(x)$, where x refers to a variable point in the dielectric x cm. distant from one plate, is introduced into the dielectric (the potential difference across the condenser being maintained at the previous value V), additional work W_e will be necessary in order to do so. W_e will be stored in the condenser above and additional to the work W_0 done in charging the loss-free condenser. The total energy stored in the condenser, W_t , is thus given by

$$W_t = W_0 + W_e \dots\dots\dots (4)$$

However, not all the energy W_t stored in the condenser which now contains free charges in its dielectric, will be free energy, since a quantity of energy W_ϕ will be bound in the space charge itself. The total energy W_t , therefore, can be written as the sum of the free electrostatic energy W_f which is available for reversible work, and the unavailable energy bound within the space charge itself, W_ϕ :

$$W_t = W_f + W_\phi \dots\dots\dots (5)$$

It should be stressed again that the potential difference across the condenser is maintained at a constant value V throughout the above operations. Combining equations (4) and (5) yields for W_f

$$W_f = W_0 + W_e - W_\phi \dots\dots\dots (6)$$

The work W_e is done against V :

$$W_e = -VD(E'_a - E_0)/4\pi \dots\dots\dots (7)$$

where E'_a is the total field existing in the presence of the space-charges at the plate which is maintained at the potential V against the other plate. E_0 is the Laplacian field in the absence of a space charge, given by

$$E_0 = -V/a \dots\dots\dots (8)$$

If a field E' is produced at a point x by the space charges, the energy bound within a space configuration of charges can be written

$$W_\phi = \frac{D}{8\pi} \int_0^a (E')^2 dx \dots\dots\dots (9)$$

Furthermore

$$dE'/dx = 4\pi\rho/D \dots\dots\dots (10a)$$

$$\int_0^a \rho dx = Q, \text{ the total charge/cm.}^2 \dots\dots\dots (10b)$$

The energy equation for the condenser containing free charges in its dielectric thus follows as

$$W_f = - \left[C_0 V^2/2 + VQ + \frac{D}{8\pi} \int_0^a (E')^2 dx \right] \dots\dots\dots (11)$$

where C_0 stands for the geometric capacity of the condenser in the absence of space charges, given by

$$C_0 = D/4\pi a = 2W_0/V^2 \dots\dots\dots (12)$$

In any actual case the term VQ in equation (11) will always be negative, since either V or Q will have to be negative, in order to maintain the space charge. The negative sign of W_f in equation (11) indicates that work equal to W_f can be done reversibly by the system.

From equation (11) the capacity and the permittivity of the charge filled dielectric follow by virtue of equations (2) and (3), once the field distribution within the dielectric is known. It is seen that the presence of a space charge leads to a diminution of the effective dielectric constant of the medium, a well known experimental fact which has been proved, e.g. for ionized gases, by Imam and Khastgir (1937). In the appendix, C and the effective dielectric constant D are calculated for a simple but representative case, viz. a plane parallel diode obeying the Child-Langmuir $3/2$ power law. D results as $3/5$, a value which has been obtained, *inter alia*, by Llewellyn (1941) from dynamical considerations. Another interesting case in point is the electric double layer confronting a polarized electrode in an aqueous solution. C_0 is negligibly small in this case, since the whole condenser comes into being only by virtue of the ionic space charge. This problem will be dealt with in a separate communication.

As W_f represents free energy capable of doing reversible work, the laws of thermodynamics are applicable, if a one-to-one correspondence can be established between a given electrical and a thermal system having the same free energy G , so that $G=W_f$. The Gibbs Free Energy G is given by

$$G=U+W-TS \dots\dots\dots (13)$$

where U is the internal energy of the system, W the work done on the system, T the absolute temperature and S the entropy.

A thermal system where $G=W_f$ can be constructed as follows :

Given a canonical distribution of elementary condensers each charged to a certain potential ψ and having an average density of charge $\bar{\rho}=\text{Const.}$, so that the total charge Q is also constant : following the standard statistical treatment (Lindsay, 1941) the entropy of the system is defined in terms of the distribution modulus θ , which has the dimension of energy and can be interpreted as the average energy of every unit cell making up the statistical ensemble. In the case of a thermal system, these unit cells are particles (say gas molecules) with an average energy of $kT/2$, measured in thermal units. In the case of an electrical system, the average energy equals $\bar{\rho}\psi/2$, measured in electrical units, and each cell represents one elementary condenser. Integrating over the whole system, its energy becomes equal to $QV/2$, where V is the potential appearing across the plates of the resulting macroscopic condenser, while the energy of the thermal system becomes equal to $RT/2$. As the energy of the electrical and that of the corresponding thermal system are equal, it follows that¹

$$QV=RT=\theta \dots\dots\dots (14)$$

An ideal gas is characterized by

$$C_p-C_v=\text{Constant}=R \dots\dots\dots (15)$$

The gas law $pv=RT$ then holds, C_p and C_v being the specific heat at constant pressure and constant volume, respectively, and p the pressure and v the volume. This is the equivalent to the restriction imposed on the electrical system by the condition that $Q=\text{Constant}$. If $Q \neq \text{Constant}$, the electric system corresponds to a non-ideal gas where equation (15) no longer holds, i.e. where $R=f(T \dots)$.

Equation (14) shows that appropriate values have to be assigned to V and T , because Q and R (for an ideal gas and its electric counterpart) are constants. Therefore, if V is given, T is uniquely determined, and *vice versa*. A one-to-one correspondence thus exists between these two quantities.

An analogue between V and T has first been proposed by Mach (1871, 1919) and Lippmann (1876). The electric-current thermal-current analogue is well known (Avrami and Paschkis, 1942) and recently Bosworth (1946) has established the thermal equivalent of the Ohm, Farad and Henry.

¹ Equation (14) in the form $V^2C/2=kT/2$ has been first used by Einstein (1907) in a treatment of the effect of Brownian motion on the potential across a condenser.

The one-to-one correspondence between V and T having been established, it also follows from equation (14) that $Q = \int_0^a \rho dx$ corresponds to R . The product $RT = pv$ thus corresponds in the electrical case to W_e .

As to the enthalpy H , the counterpart of the total energy W_t of the electrical system, it can be written

$$H = U + W \dots\dots\dots (16)$$

Since it has been shown that $W = pv = RT$ corresponds to $W_e = QV$, U is seen to be in one-to-one correspondence with W_o , since the electric and the corresponding thermal system are to have equal energy. W_o electrically also behaves similarly to U in a cyclic process, because it returns to its initial value when V (or T in the thermal case) is first increased and then allowed to return to its former value. In other words, the internal energy in the thermal case is a single valued function of T exactly as the energy stored in the geometric capacitance of a condenser is a single valued function of the potential to which it is charged. It is now seen that the term TS in the thermal case, equation (13), corresponds to the term W_ϕ in the electric system described in equation (6). Since T has been shown to be in one-to-one correspondence to V , the quantity W_ϕ/V , which it is proposed to call the ELECTRICAL ENTROPY, similarly corresponds to the thermal entropy S . More accurately, the differential change in the electrical entropy dS_e , defined by

$$dS_e = \frac{dW_\phi}{V} \dots\dots\dots (17)$$

is in one-to-one correspondence to the entropy element

$$dS = \frac{dq}{T} \dots\dots\dots (18)$$

For a rigid proof that equation (17) represents an entropy element it must be shown (1) that dW_ϕ is not an exact differential, and (2) that $1/V$ is an integrating factor making dW_ϕ/V exact.

Since W_ϕ is a function of V , $\oint W_\phi dV$ would vanish if dW_ϕ were exact. From equations (4) and (5) W_ϕ can be written

$$W_\phi = W_t - W_f \dots\dots\dots (19)$$

If $\oint W_\phi dV = 0$ would hold, $\oint W_t dV$ would vanish also, since $\oint W_f dV$ vanishes by definition of W_f as free energy available for reversible work. But in general

$$\oint W_t dV \neq 0 \dots\dots\dots (20)$$

since work might be done on or by the system. Therefore contention (1) is proved.

As to the second proposition, it must be shown that

$$\oint \frac{dW_\phi}{V} = 0 \dots\dots\dots (21)$$

Again, since $\oint W_f dV = 0$, equation (21) can be written, using equation (5), thus :

$$\oint \frac{W_e}{V} dV = 0 \dots\dots\dots (22)$$

Assume that this were not true. It then would be possible by repeating the cyclic process of first increasing and thereafter decreasing V to its initial value, to increase the total space charge Q without limit (always assuming the potential changes to be slow compared with the relaxation time of the process, or in other words slow enough to allow the charge distribution to come into equilibrium for all intermediate values of V). This would be against experience and against the laws of thermodynamics. The proposition, therefore, is proved.

The electrical entropy of an electrostatic system where $Q = \text{constant}$ follows directly from the statistical considerations on page 68 and equation (14), as

$$(S_e)_{Q=\text{const}} = Q \log (V/N!) \dots\dots\dots (24)$$

where N is the number of unit cells comprising the statistical ensemble, and therefore an additive constant. Equation (24) is thus seen to be formally identical with the Boltzmann relation

$$S = k \log w + \text{const} \dots\dots\dots (25)$$

where w is a measure of the probability of the system to be found in a state determined by the energy of the statistical canonical distribution modulus θ .

Furthermore, it is seen that the electrical entropy thus comes within the scope of definition of entropy as a measure of the extension of an equilibrium state, as given by Postma (1916). Equation (24) can also be derived from equation (17), which can be written

$$dS_e = \frac{1}{V} \frac{dW_\varphi}{dV} dV \dots\dots\dots (26)$$

for $Q = dW_\varphi/dV = \text{Constant}$.

Table 1 lists the two sets of quantities shown to be in one-to-one correspondence with each other:

TABLE 1.

| Electrical Quantity. | Thermal Quantity. |
|---|--|
| Free electrostatic energy W_f . | Gibbs' free energy G . |
| Energy stored in condenser in the absence of space charges, W_0 . | Internal energy U . |
| Work done in introducing the space charges, W_e . | Work done by or against external forces, W . |
| Potential V . | Temperature T . |
| Volume of the condenser v . | Volume of the gas v . |
| Energy bound in the space charge, W_φ . | TS . |
| The product potential V by average space charge density ρ . | Average pressure of the gas, \bar{p} . |
| Total energy W_t . | Enthalpy H . |
| Total charge $Q = \int \rho dv$. | Gas constant $R = C_p - C_v$. |
| Electrical entropy dW_φ/V . | Entropy dq/T . |

All the electrical quantities are time-variable to the extent that V is a function of time. Moreover, if a cyclic process is considered by first increasing V to a predetermined value and then reducing it again to its initial value, then the time taken for such a cycle must be large compared with the relaxation time of the readjustment of the system to the altered field. This is the exact counterpart to the thermal case where in an isochoric cycle the change of T must not be too fast for the thermal conductivity of the gas. In both cases, the rate of change of T or V , respectively, must be sufficiently small to permit consideration of the whole gas or dielectric as in a state of thermal or electrical equilibrium for every intermediate value of T or V . Since the temperature T represents an absolute, irreducible, dimensional quantity which enters into the dimensions of thermal quantities, it is clearly impossible to bring all thermal and the corresponding electric units to the same dimensions. The electric quantities, in the electrostatic system, are based upon the permittivity of free space, which enters into their dimensional formulae and which equally represents an absolute and irreducible dimensional quantity. However, there are some cases where the corresponding electric and thermal quantities also have the same dimension, even if that cannot

be expected in general. The pressure \bar{p} and $\bar{\rho}V$ present such an exceptional case, having the same dimension ($ml^{-1}t^{-2}$).

The second law of thermodynamics can now be applied to a purely electrical system :

EVERY PURELY ELECTRICAL PROCESS WILL TAKE PLACE IN SUCH A MANNER THAT THE ELECTRICAL ENTROPY OF THE SYSTEM INCREASES.

This can take place either by the increase of the bound energy W_ϕ , by the decrease of the potential difference V , or by a combination of both processes. Moreover, in correspondence to the thermal case, $dS_e = V^{-1}dW_\phi$ is an exact differential and the electrical entropy completely and uniquely describes the electrical state of the system.

The following examples might serve to illustrate the application of this law :

- (i) A SOLID DIELECTRIC UNDER ELECTRIC STRESS HIGH ENOUGH TO PRODUCE IONIZATION :

Once ionization sets in, i.e. free charges appear, the dielectric constant of the medium decreases (Imam and Khastgir, 1937) (W_ϕ increasing and W_t therefore decreasing). At the same time the conductivity of the dielectric increases (the potential V across it is lowered unless maintained from outside), as is well known.

- (ii) A REVERSIBLE ELECTRODE REACTION :

Increase of concentration of dischargeable ions (i.e. increase of free charges) reduces the discharge potential (V decreases). At the same time a higher potential is needed before the limiting current is reached because a greater proportion of the energy supplied, W_t , is transformed into unavailable energy W_ϕ . Both effects are well known experimental facts (Kolthoff and Lingane, 1941).

The entropy of a perfect monatomic gas is given by

$$S = \frac{5}{2}R \log T - R \log \bar{p} + \text{Const.} \dots\dots\dots (27)$$

In the corresponding electrical system this becomes, by virtue of equivalences listed in Table 1,

$$S_e = \frac{5}{2}Q \log V - Q \log \bar{\rho}V + \text{Const.} \dots\dots\dots (28)$$

$$= \frac{3}{2}Q \log V - Q \log \bar{\rho} + \text{Const.} \dots\dots\dots (29)$$

The average charge density $\bar{\rho}$ in the electrical counterpart of a perfect gas being constant (see page 68, equations (14) and (15) and following), equation (29) can be expressed thus :

$$S_e = \frac{3}{2}Q \log V + \text{another constant} \dots\dots\dots (30)$$

A monatomic gas having three degrees of freedom, the electrical entropy of the corresponding electrical system, *per degree of freedom*, results as

$$S_{e/t} = \frac{Q}{2} \log V + \text{Constant} \dots\dots\dots (31)$$

However, the space charge element in a plane parallel condenser has only two degrees of freedom of translatory motion, which also follows from Gibb's Phase Rule : If C is the minimum number of components required to describe each phase of the system completely and P is the number of phases, the degrees of freedom F are given by

$$F = C - P + 2 \dots\dots\dots (32)$$

Thus in the electric system $P=2$, corresponding to free energy and bound energy and C is equal to 2, corresponding to the charge and the potential, describing each phase. F therefore equals 2. The total electrical entropy of an electrical system where $Q=\text{Constant}$, therefore follows as

$$S_e = Q \log V + \text{Constant} \dots\dots\dots (33)$$

This equation thus has been derived from purely thermodynamical considerations by application of the one-to-one correspondences listed in Table 1. As can be seen, equation (33) is identical with equation (24), which was derived directly from the statistics of the electrical system. This, then, is an example for the correctness of applying thermodynamic reasoning to electrical processes.

If the potential V on one plate of the condenser is reduced to another value V' , a certain amount of energy W_ϕ will not appear as available energy, but will be dissipated or irreversibly expended. In parallelism to a thermal process, W_θ can be calculated from the electrical entropy S_e :

$$W_\phi = V' \int_{V'}^V \frac{1}{V} dW_\phi = V' \int_{V'}^V F\left(x, V, \frac{dV}{dx}\right) dx \dots\dots\dots (34)$$

It is of interest to find some conditions which make W_θ vanish or a minimum $\neq 0$. It is obvious that if $W_\theta=0$ or $V'=0$, W_θ also will vanish. The former case is trivial, since it amounts to a condenser without space charge. The latter can be realized only by connecting the condenser plates for a time sufficient to allow *complete* discharge. It is known, however, from the phenomenon of dielectric absorption that the rate of decay of W_ϕ in general even after the removal of V is slow (Gross and Denard, 1945). To find the conditions which make W_θ a minimum $\neq 0$, Euler's equation is set up for the path which makes the integral in equation (34) a minimum:

$$\frac{\partial^2 F}{\partial \rho \partial \rho} + \frac{\partial^2 F}{\partial V \partial \rho} \frac{dV}{dx} + \frac{\partial^2 F}{\partial \rho^2} \frac{d^2 V}{dx^2} = 0 \dots\dots\dots (35)$$

where $F = F\left(x, V, \frac{dV}{dx}\right)$ and $p = -dV/dx$. In the present case, $F = \frac{(E')^2}{V}$

and $p = -dV/dx = (E' + E_0)$. It is seen that $F = \text{Const.}$ is one solution of equation (35). This is the special case of a dielectric where

$$(E')_a = \frac{4\pi Q}{D} = \text{Const. } V^{\frac{1}{2}} \dots\dots\dots (36)$$

The connection between this condition and the well-known Debye-Hueckel equation will be dealt with in a separate communication.

Another solution of equation (35) is $p = \text{Constant}$:

$$\begin{aligned} dV/dx &= \text{Constant} \\ V &= \text{Const.} \cdot x + \text{Constant} \dots\dots\dots (37) \end{aligned}$$

i.e. a linear relationship between local potential V and x , or, therefore, the condition that the *total* potential is Laplacian. The system thus will operate under minimum energy dissipation if the externally applied field E_0 and the field due to the space charges cancel at the condenser plates, i.e. when the system is in potential equilibrium at the plates. This is possible only in a region of space charge where $E_0 = -4\pi Q/D$. This is equivalent to $dQ/dV = \text{Const.}$, which plays a similar role to the specific heat in thermal processes. For the reversibility of the electric process, therefore, it is sufficient if the *total* space charge present is either constant or linearly proportional to the potential across the condenser. This condition does not imply a purely static case, i.e. the absence

of a space-current : it suffices if $\text{div } (\partial \rho / \partial t)$ is either constant or linearly proportional to V . In other words, a dielectric may contain free charges and still be loss-free, subject to the above conditions. Physically, these can be interpreted as meaning that for minimum electrical waste energy the field at the plate must be in equilibrium with the field of all space charges in the dielectric. Such systems actually exist in nature ; they are approached in electro-chemical reactions, in the region in front of the plate (or in the space between plate and suppressor) of a pentode, where the plate current is nearly independent of the plate potential, and also by a triode biased to cut-off, so that the field due to the grid, plate and electrons exactly balance.

The capacity defined in equation (2) represents the d - c capacity measurable after a steady state has been attained. For varying and for alternating potentials a capacity C_d is defined by the differential

$$C_d = dq_0 / dV \\ q_0 = 2W_t / V \dots\dots\dots (38)$$

q_0 being the free charge. Since the derivative dQ/dV enters into the expression for C_d , it is seen that the *change* in the free energy and with it C_d , depend on the relaxation time of Q . In other words, the ideally reversible free charge is truly so only for infinitely small (i.e. infinitely slow) changes of V , since it will always take a finite time for Q to adjust itself to a change in V . This time, as has been pointed out by Gross and Denard (1945), may be extremely long, in some cases even hundreds of thousands of years. It is another example of processes, so well known to thermodynamics and chemical kinetics, processes which are only partly reversible in practice, while in themselves they are inherently completely reversible reactions.

III. SUMMARY.

The free electrostatic energy, capable of doing reversible work, stored in a space-charge filled condenser, is calculated, yielding an expression for the effective dielectric constant of a medium containing free charges.

A one-to-one correspondence between a number of thermal and electrical quantities is established. The electrical entropy S_e is defined as $dS_e = V^{-1}dW_\phi$, V being the potential difference across the condenser and W_ϕ the energy bound within the space configuration of charges. It is proved that dS_e is an exact differential. The second law of thermodynamics is applied to purely electrical systems in the form : Every purely electrical process will take place in such a manner that the electrical entropy of the system increases.

Further equivalences between electrical and thermal processes are demonstrated. It is shown that a space charge filled condenser may still be loss free, if the sum total of the free charges in its dielectric is constant or linearly proportional to the potential difference across the condenser.

IV. ACKNOWLEDGEMENTS.

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V. APPENDIX.

The Child-Langmuir 3/2 power law for a plane parallel diode can be written thus (Koller, 1937) :

$$V = \left[\frac{Jx^{2/3}\pi}{(2e/m)^{1/2}} \right]^{2/3} \dots\dots\dots (39)$$

where J is the space current density, x a variable point where a local potential V exists (at the plate, $x=a$, the interelectrode spacing and $V=V_0$ the plate voltage), and e/m the specific electronic charge. The space charge being in *vacuo*:

$$\frac{D}{8\pi} \int_0^a (E')^2 dx = \frac{1}{8\pi} \frac{16\pi(9\pi)^{1/3} J^4 /_3 a^5 /_3}{(2e/m)^2 /_3} \frac{3}{5} \dots\dots\dots (40)$$

Since

$$\rho = V/v = \frac{J V^{-1/2}}{(2e/m)^{1/2}} \dots\dots\dots (41)$$

where v is the average local velocity of the electrons, given by

$$mv^2/2 = eV \dots\dots\dots (42)$$

Q results as

$$Q = \int_0^a \rho dx = \frac{J}{(2e/m)^{1/2}} \int_0^a V^{-1/2} dx \dots\dots\dots (43)$$

But from equation (39):

$$V^{-1/2} = \left[\frac{Jx^2 9\pi}{(2e/m)^{1/2}} \right]^{-1/3} \dots\dots\dots (44)$$

Therefore

$$Q = \frac{J}{(2e/m)^{1/2}} \int_0^a \left[\frac{9\pi J}{(2e/m)^{1/2}} \right]^{-1/3} x^{-2/3} dx \dots\dots\dots (45)$$

yielding on integration

$$Q = \frac{J^2 /_3 3a^{1/3}}{(9\pi)^{1/3} (2e/m)^{1/3}} \dots\dots\dots (46)$$

Recalling equations (2), (11) and (12) for C , W_t and C_0 respectively, it follows on substitution that

$$D = C/C_0 = -1 + \frac{8}{3} - \frac{16}{15} \frac{3}{5} \dots\dots\dots (47)$$

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THE EFFECT OF pH UPON THE ULTRA-VIOLET ABSORPTION SPECTRA OF PYRIDINE TYPE COMPOUNDS.

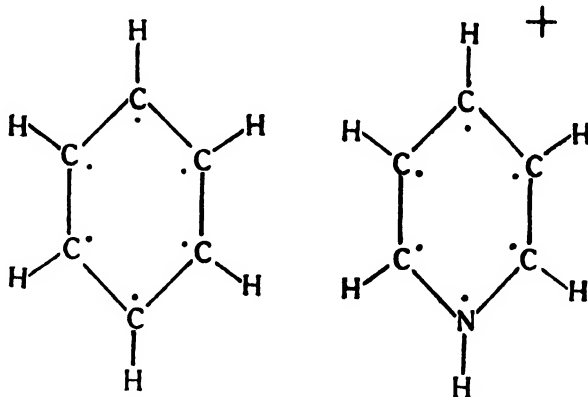
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INTRODUCTION.

Previous studies by Loofbourov and Stimson (1940) and Craig and Short (1945) have shown that the ultra-violet absorption of such N-containing substances as barbituric acid, guanine, adenine and the various aminoacridines changes with pH. An explanation for the former group has been given in terms of tautomers and for the second in terms of ions.

The present study was undertaken with a view to determining the molecular species present at different pH's, to assist in the interpretation of polarographic curves, but the results may be of interest to those concerned in the theoretical investigation of the energies of molecular π -orbitals, as the introduction of H^+ into, say, pyridine adds no electrons and gives a resultant molecule which in some ways resembles benzene, having a similar distribution of nuclei :



The difference from benzene is twofold : (i) the symmetry of the molecule is lessened by the presence of N instead of a C ; and (ii) an excess positive charge is present. The effect of (i) would be expected as a blurring of the vibrational partial band structure and of (ii) as an alteration in the energies of the molecular orbitals, necessitating different values given to certain integrals in the theoretical treatment, and being revealed in a shift in the wave number of the corresponding band. Furthermore, it was thought possible that the results might throw some light on vibrational modes of the free base molecules.

EXPERIMENTAL.

All measurements were made on a Beckmann ultra-violet spectrophotometer with a hydrogen discharge lamp as light source. Each substance used was dried and purified by either repeated fractionation or crystallization.

The strength of all solutions was 10^{-4} M.

RESULTS.

The results are graphed and tabulated, together with some values in hydrocarbon solvents obtained from the literature.

ϵ is defined by the relation $I = I_0 10^{-\epsilon cd}$

where I , I_0 are transmitted and incident light intensities,

c is molar concentration,

d is cell thickness (cm.).

DISCUSSION OF RESULTS.

1. The formation of the $\equiv\text{NH}^+$ ion at pH 4 from the free base, $\equiv\text{N}$, is consistent with the results, as will be seen from the following; which means that the absorption at the lower pH is in every case by a molecular species different from that which absorbs at pH 7. A further change of pH from 7 to 10 should accordingly produce no further change in the nature of the absorption. This was tested, and the results were as expected except that with quinaldinic acid there was a slight difference in the absorption curves at pH 7 and 10. However, this is easily explicable in view of the presence of the carboxyl group and its possible ionization as well as a certain amount of zwitterion formation. Thus the results confirm the attribution of the spectral differences to the presence of different molecules and conversely enable the latter to be identified from the spectra.

2. The differences in spectra at pH's 4 and 7 are of two sorts: (a) a change in ν_1 , the wave-number of the first maximum, i.e. the maximum corresponding to the least possible energy difference in a transition between lower and upper states of the absorbing molecule, and in which a minimum of the absorbed energy is used to excite higher vibrational levels in the upper state; and (b) a change in the intensity of absorption measured by ϵ , and in particular a change in ϵ_1 , the value at ν_1 .

TABLE 1.

| Substance. | Solvent. | ν_1 . | ϵ_1 . | ν_2 . | ϵ_2 . | ν_3 . | ϵ_3 . |
|---------------------|----------------|-----------|----------------|-----------|----------------|-----------|----------------|
| Pyridine(1) | pH 4. | 39,150 | 5,200 | > 40,500 | — | — | — |
| " | pH 7. | 39,200 | 2,650 | 39,840 | 2,400 | > 40,500 | — |
| " | Iso-octane(2). | 39,100 | 1,660 | 39,600 | 1,760 | — | — |
| Quinoline(1) | pH 4. | 32,050 | 5,850 | — | — | — | — |
| " | pH 7. | 32,050 | 2,950 | 33,300 | 3,100 | 35,700 | 3,280 |
| " | Hexane(3). | 32,100 | 6,310 | — | — | — | — |
| Iso-quinoline(1) .. | pH 4. | 30,200 | 4,200 | 37,040 | 2,220 | > 40,500 | — |
| " | pH 7. | 31,450 | 2,560 | 32,570 | 2,220 | 37,750 | 3,080 |
| " | Hexane(3). | 31,700 | 3,160 | — | — | — | — |
| Quinaldine(1) | pH 4. | 31,750 | 7,300 | > 40,500 | — | — | — |
| " | pH 7. | 33,170 | 3,600 | 36,100 | 3,500 | — | — |
| Quinaldinic acid(1) | pH 4. | 31,250 | 6,550 | > 40,500 | — | — | — |
| " | pH 7. | 34,400 | 4,250 | > 40,500 | — | — | — |
| 2-picoline(1) | pH 4. | 38,050 | 7,200 | 38,300 | 7,200 | — | — |
| " | pH 7. | 38,250 | 4,860 | — | — | — | — |

(1) At pH 4 will be in the form of the ion.

(2) American Petroleum Institute Research Project 44, National Bureau of Standards Catalog of Ultraviolet Spectrograms, Serial No. 108.

(3) International Critical Tables, V (1929).

3. Changes in ν_1 did not occur in the cases of pyridine, 2-picoline and quinoline but did occur in every other case as a shift towards the red with change of pH from 7 to 4. The magnitude of the shift varied, although that in quinaldine was equal to that in iso-quinoline. It is unlikely that the quinaldine acid shift which is far greater than either of the latter two is comparable because of the obliteration of all the partial band structure in the quinaldine acid spectrum at pH 7 and consequent measurement of ν_1 , at a higher value than that corresponding to a transition to the lowest possible vibrational level of the upper state. The increasing blurring of structure is consistent with introduction of progressively more massive groups into the quinoline nucleus in the order $-\text{H}$, $-\text{CH}_3$, $-\text{COOH}$. No explanation can be advanced at present for the similarity of the shift in the cases of quinaldine and iso-quinoline.

The similarity of ν_1 for pyridine (2-picoline, quinoline) and its ion means that the introduction of a hydrogen nucleus and of a positive charge into the molecule has the same effect on the energy of each level concerned in the transition, thus preserving a constant difference between the two. It does not necessarily mean that the introduction of a positive charge is without any effect on the potential energy of the molecular orbitals; it would be remarkable if this were so, since it would imply that the field in which the electrons moved was unaffected by the increased nuclear charge.

4. Change in ϵ_1 was invariably an increase as the pH changed from 7 to 4. The values of R [$=(\epsilon_1)_{\text{pH } 4} : (\epsilon_1)_{\text{pH } 7}$] are given in Table 2.

TABLE 2.

| Substance. | | | | | R |
|-----------------|----|----|----|----|-----------|
| Pyridine | .. | .. | .. | .. | 1.98 |
| 2-picoline | .. | .. | .. | .. | 1.50 |
| Quinoline | .. | .. | .. | .. | 1.98 |
| Iso-quinoline | .. | .. | .. | .. | 1.63 |
| Quinaldine | .. | .. | .. | .. | 2.03 |
| Quinaldine acid | .. | .. | .. | .. | (1.70)(1) |
| Acridine(2) | .. | .. | .. | .. | 2.2 |
| Mean | .. | .. | .. | .. | 1.9 |

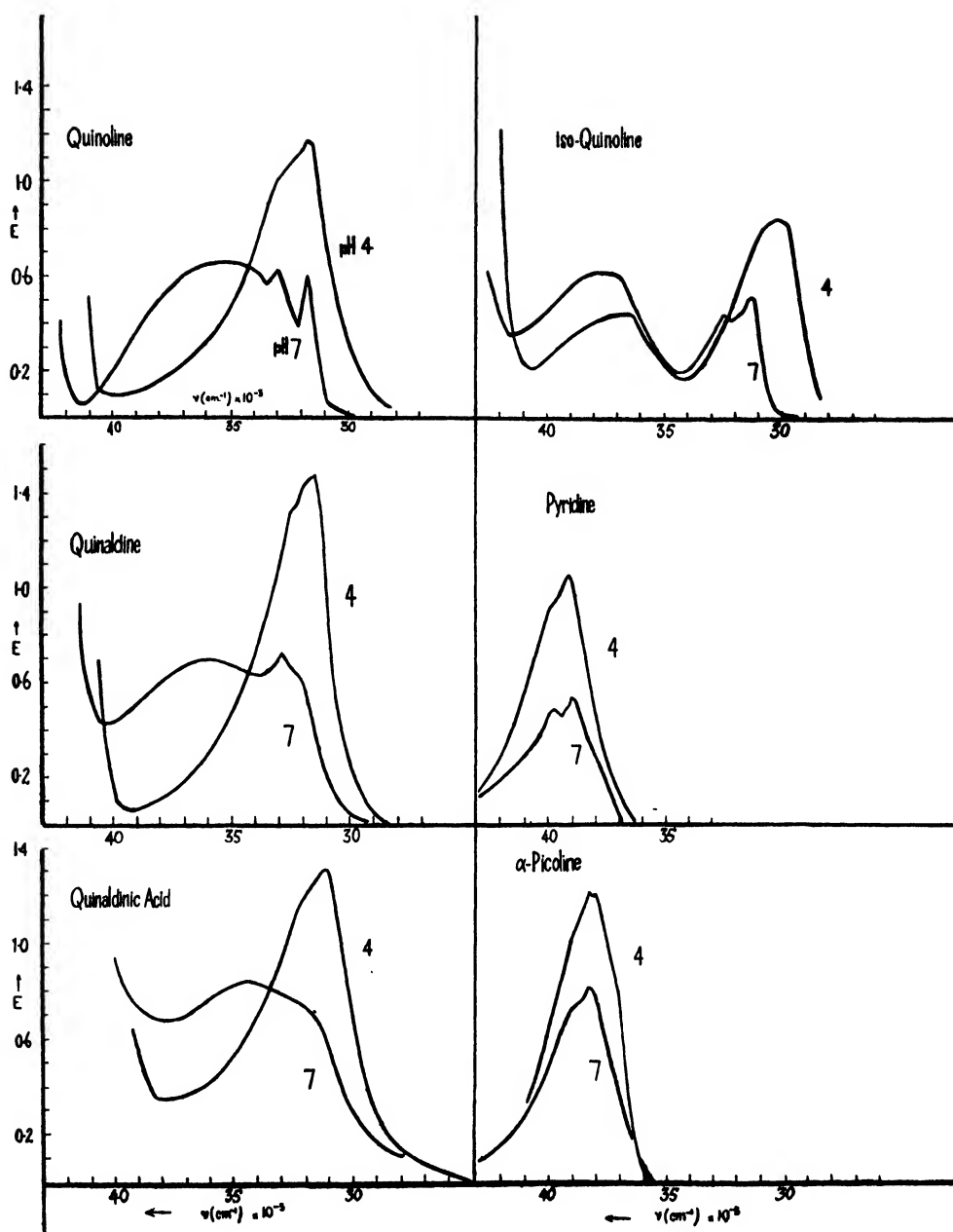
(1) This figure is not strictly comparable for the reason mentioned above and is omitted from the mean.

(2) Calculated from graphs of Craig and Short (1945).

Although a better method of measuring the intensity of absorption is by the area enclosed by the curve, the values obtained for R show clearly the general trend and the closeness of the values for pyridine, quinoline and quinaldine is especially interesting, as is the similarity of the absolute value of ϵ_1 for pyridine and quinoline, indicating that the fusion of a benzene ring with a pyridine ring is without effect upon the intensity of short wave-number absorption despite the shift in the location of the absorption.

5. ϵ at other wave-numbers was in every case greater over a considerable range at pH 7 than at pH 4. However, the total absorption as measured by the

area $\int_{\nu=0}^{40,000 \text{ cm.}^{-1}} \epsilon d\nu$ was always about 25% greater at pH 4 than at pH 7.



It is hoped to consider the spectra of these molecules from a theoretical point of view at a later date.

6. By noting the pH at which the absorption changes from that of $\equiv\text{NH}^+$ to that of $\equiv\text{N}$ a method is available for determining the pK value of $\equiv\text{NH}^+$ compounds.

SUMMARY.

The ultra-violet absorption spectra of pyridine (I), 2-picoline (II), quinoline (III), quinaldine, quinaldinic acid and iso-quinoline have been measured in buffered aqueous solutions of known pH. In every instance the absorption at pH 4 differed from that at pH 7 in that the intensity of the long wave-length band was increased by a factor of approximately two and, except for I, II and III, was shifted from the red. This behaviour is attributed to the formation of the ion at pH 4.

The introduction of H^+ into I, II and III affects equally the energies of the two molecular orbitals concerned in a transition, but this is not so with the other three compounds.

The method of ultra-violet absorption spectra is suited to the determination of pK values for pyridine type compounds.

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PART II

NITROGEN IN OIL SHALE AND SHALE OIL.

X. NITRILES IN SHALE OIL.

By GEO. E. MAPSTONE, M.Sc., A.A.C.I., A.R.I.C., M.Inst.Pet.

Manuscript received, April 10, 1949. Read, June 1, 1949.

INTRODUCTION.

The only nitrogen compounds that have yet been isolated and identified from shale oil are pyridine homologues, though pyrroles have also been identified as a class (Mapstone, 1948a). Apart from these, and the presence of possible traces of primary amines (Mapstone, 1948a), no other classes of nitrogen compounds appear to have been detected in crude shale oils. This is probably due to the difficulty of isolating and examining the weakly basic and non-basic nitrogen compounds from the oil, even though less than 20% of the nitrogen present in crude shale oil is sufficiently basic to be extracted by dilute acids. It is of interest that more than 20% of the nitrogen is not extracted even by concentrated sulphuric acid (Mapstone, 1948e).

A review of the pyrolytic reactions that may be involved in the carbonisation of oil shale to produce crude shale oil, suggested that nitriles may be present in the oil in small amounts (Mapstone, 1948c, 1948d). The work described in this paper was carried out in an attempt to detect nitriles as a class in crude shale oil.

HYDROLYSABLE NITROGEN IN CRUDE SHALE OIL.

Previously, it had been found that the distillation of the oil with caustic soda solution required several hours before all the ammonia was distilled (Mapstone, 1945). This prolonged treatment would cause hydrolysis of any amides or nitriles, and the total ammonia evolved would be that from these sources, as well as that from free ammonia and ammonium salts initially present in the oil. At the same time, some of the lower boiling pyridine homologues present could be expected to distil along with the small amount of oil which came over with the ammonia and steam, and these would be recorded as ammonia. The original method was therefore modified, and the different factors examined in turn.

The proportion of oil distilling with the steam was reduced appreciably by using a fractionating column. In this respect a twelve pear column, although slightly more efficient than a four pear column, increased the time required for the distillation between two- and three-fold. By using a low heating rate, the fractionating column acted as a reflux condenser. Handling losses, etc., were greatly reduced by gently refluxing the oil with the caustic soda solution for a while, and then distilling off the ammonia with a fair amount of steam at a faster rate.

In the absence of an antifoaming agent, it was almost impossible to carry out a test. Cresylic acid was a very effective antifoaming agent, and better than amyl or butyl alcohols, which, though effective at the start, passed over with the steam during the distillation, so that serious foaming was sometimes experienced near the end of the test.

Between 50% and 60% of the tar bases present in the oil which distilled with the ammonia and water were extracted by the boric acid and titrated as ammonia. The oil distillate recovered from a series of tests using unwashed crude shale oil contained approximately 0.045% by weight of basic nitrogen.

Once the principle of the analytical method was established, a series of analyses was carried out, using the same sample of crude oil. The results obtained decreased steadily throughout the series from about 130 to 60 p.p.m. by weight of nitrogen in the oil. This decrease was shown to be most probably due to loss of free ammonia by the reduction of the hydrolysable nitrogen content of a fresh sample of oil from 132 to 55 p.p.m. by bubbling with air overnight.

EFFECT OF ACID WASHING ON HYDROLYSABLE NITROGEN.

Preliminary experiments indicated that, even in the absence of ammonia, the hydrolysable nitrogen content of the crude shale oil was reduced by washing the oil with dilute acids (Table I). A further series of experiments was therefore carried out by acid washing solutions of various nitriles and of oleamide in acetic acid-washed crude shale oil.

TABLE I.
Acid Washing Crude Shale Oil.

| Acid. | Amount of Acid. | Washing Time. | Water Wash. | Hydrolysable Nitrogen. (Parts per Million.) |
|--------------------------|-----------------|---------------------|-----------------------|---|
| Nil | — | — | — | 90 |
| Acetic 5% | 400 ml./l. | $\frac{1}{2}$ hour. | Nil. | 56 |
| Acetic 5% | 400 ml./l. | $\frac{1}{2}$ hour. | 500 ml./l. | 72 |
| Acetic 5% | 400 ml./l. | 16 hours. | Nil. | 60 |
| Acetic 5% twice | 400 ml./l. | $\frac{3}{4}$ hour. | 500 ml./l. | 47 |
| Acetic 25% | 150 ml./l. | $\frac{1}{2}$ hour. | 500 ml./l. | 37 |
| Acetic 25% twice | 150 ml./l. | $\frac{3}{4}$ hour. | 500 ml./l. | 28 |
| Acetic 25% | 150 ml./l. | 17 days. | 500 ml./l. | 26 |
| Acetic glac. | 10 ml./l. | $\frac{1}{2}$ hour. | 2 \times 500 ml./l. | 56 |
| Acetic glac. twice | 10 ml./l. | $\frac{3}{4}$ hour. | 2 \times 500 ml./l. | 53 |
| Acetic glac. | 10 ml./l. | 16 hours. | 2 \times 500 ml./l. | 53 |
| Sulphuric 5% | 400 ml./l. | 1 hour. | Nil. | 34 |
| Sulphuric 5% | 400 ml./l. | 1 hour. | 500 ml./l. | 38 |
| Sulphuric 5% | 400 ml./l. | 16 hours. | 500 ml./l. | 28 |
| Sulphuric 10% | 170 ml./l. | 1 hour. | 500 ml./l. | 34 |
| Sulphuric conc. | 40 ml./l. | 1 hour. | 3 \times 500 ml./l. | 35 |

The results obtained (Table II) indicated that the most of any acetonitrile present was removed by the washing. As the molecular weight of the nitriles increased, the proportion extracted by the dilute acids generally decreased, although benzyl cyanide was the least extractable of the nitriles examined. Oleamide was several times as readily extracted as cetyl cyanide, a difference which appears due to the difference in the properties of the polar groupings rather than in the hydrocarbon chains.

By washing with 5% sulphuric acid and separating immediately, and then washing another portion of the sample and leaving it in contact with the acid overnight, it was hoped that some measure of the amount of hydrolysis occurring during the washing could be obtained. The results (Table II) suggested that there was little, if any, hydrolysis at the oil-acid interface.

TABLE II.
Effect of Acid Washing on Nitriles in Crude Shale Oil.

| Organic Cyanide Added. | Nil. p.p.m. N. | Acid Treatment. | | | | | |
|------------------------|-------------------|---|------------|---|------------|--|------------|
| | | 250 ml./l. of 5% H ₂ SO ₄ then H ₂ O. | | 250 ml./l. 5% H ₂ SO ₄ overnight then H ₂ O. | | 50 ml./l. glac. HAc then 2 × 500 ml./l. of H ₂ O. | |
| | | p.p.m. N. | % Loss. | p.p.m. N. | % Loss. | p.p.m. N. | % Loss. |
| Unwashed oil | 97 | — | — | — | — | — | — |
| Washed oil | 31 | 26 | 16 | 19 | 39 | — | — |
| Benzyl | 564 | 520 | 6 | 557 | 1 | 570 | 1 |
| Methyl | 1300 | 271 | 79 | 170 | 87 | 43 | 97 |
| Butyl | 248 | 145 | 42 | 180 | 27 | 138 | 44 |
| Cetyl | 41 | 34 | 17 | 31 | 24 | 37 | 10 |
| Cetyl | 94 | 81 | 14 | 78 | 17 | 85 | 10 |
| Oleyl amide | 776 | 188 | 76 | 216 | 72 | 253 | 67 |

MILD REDUCTION OF CRUDE SHALE OIL.

If the hydrolysable nitrogen compounds in the crude shale oil were nitriles, reduction of the oil should decrease or even eliminate them. Because it was neutral and would therefore not hydrolyse the nitriles during the reduction, aluminium amalgam was chosen as the reducing agent.

As a preliminary test, four litres of acetic acid washed crude shale oil were refluxed for eight hours with 121 grammes of amalgamated aluminium strip. The hydrolysable nitrogen contents of the washed oil, the reduced oil, and the reduced oil plus 1.6 ml./l. of aceto nitrile were determined, together with the effect of a mild acid wash. The results (Table III) indicate a significant reduction of the hydrolysable nitrogen content of the oil, and that the remaining compounds were more readily extracted with acid.

TABLE III.
Effect of Reduction of Oil by Aluminium Amalgam.

| Oil Treatment. | Nil. | Acid Treatment. | | | | | |
|---|------|--|------------|--|------------|---|------------|
| | | 250 ml./l. 5% H ₂ SO ₄ then H ₂ O wash. | | 250 ml./l. 5% H ₂ SO ₄ overnight then H ₂ O wash. | | 50 ml./l. glac. HAc. then 2 × 500 ml. H ₂ O. | |
| | | p.p.m. N. | % Loss. | p.p.m. N. | % Loss. | p.p.m. N. | % Loss. |
| Washed crude oil .. | 47 | 31 | 34 | 38 | 19 | 40 | 15 |
| Washed crude oil re- fluxed over Al-Hg .. | 29 | 16 | 45 | 12 | 59 | 18 | 38 |
| Reduced crude oil plus some aceto nitrile .. | 521 | 367 | 29 | 238 | 54 | 149 | 71 |

A further experiment was carried out in which a slow stream of air was passed through four litres of unwashed crude shale oil refluxing over aluminium

amalgam, and then through a solution of boric acid. Samples of the oil were withdrawn each four hours, and the hydrolysable nitrogen content determined. No ammonia was evolved during the progress of the reduction. After one sample of crude oil had been refluxed with the aluminium amalgam for 24 hours, some benzyl cyanide was added (5 ml. to 3.2 l.) and the refluxing continued. The results obtained (Table IV) showed that the hydrolysable nitrogen content of the oil was reduced appreciably by the treatment, and that the rate of reduction decreased with time. This is consistent either with decreasing activity of the amalgam or with the initial more rapid reduction of some of the more reactive hydrolysable nitrogenous compounds. The results after the addition of the benzyl cyanide were inconclusive.

TABLE IV.
Reduction of Hydrolysable Nitrogen by Aluminium Amalgam.
Results in p.p.m. of Hydrolysable Nitrogen.

| Oil Sample. | Time Refluxed with Aluminium Amalgam. | | | | | |
|---|---------------------------------------|----------|----------|-----------|-----------|-----------|
| | Nil. | 4 Hours. | 8 Hours. | 12 Hours. | 16 Hours. | 24 Hours. |
| (i) Unwashed crude oil | 104 | 67 | 40 | — | — | — |
| (ii) Unwashed crude oil | 47 | 37 | 35 | 34 | — | 33 |
| (iii) Crude oil from (ii) plus some added benzyl cyanide .. | 101 | 99 | 98 | — | 96 | — |

The reduction of the nitriles should give rise to primary amines, and the detection of these in increased amounts in the crude shale oil after reduction with the aluminium amalgam would confirm the presence of nitriles in the oil. The 10 to 40 p.p.m. reduction in the hydrolysable nitrogen content of the oil obtained should be a measure of the amount of primary amine produced. This was far too small an amount of amines to be determined quantitatively, as the basic nitrogen content of the oil is of the order of one thousand times as much.

McKee claimed to have detected traces of primary amines in shale oil with nitrous acid (Mapstone, 1948a; McKee, 1925) and Horne, Finley and Hopkins obtained similar results using the carbylamine reaction (Mapstone, 1948a; Horne, Finley and Hopkins, 1938). Since the latter test seemed to be the better of the two, it was applied to samples of the crude shale oil which had been treated in various manners. Because of the very low amount of amine being sought, the samples were submitted to a jury of nine for comment. They were asked to classify the results as positive, possible, or negative, and no one was allowed to know either the history of any sample or any previous verdict until he had given his own decision.

The results of the tests (Table V) indicated a fair divergence in sensitivity of smell of the different "jurymen", but all knew the odour of carbylamine beforehand, and no one gave all results negative. The only sample on which the opinion was unanimous was that which had been washed with acetic acid, and which would, therefore, contain no basic compounds. The results suggest that refluxing the oil with aluminium amalgam did increase the primary amine content of the oil very slightly from a "possible" trace to a "probable" trace. Weathering the oil had little effect on the primary amine content, but refluxing with solid caustic potash or hydrolysis with caustic soda solution reduced it, which may have been due to the loss of volatile amines during the treatment.

TABLE V.
Results of Carbylamine Test on Various Samples of Crude Shale Oil.
(Summary of nine opinions.)

| Shale Oil Sample. | Positive. | Possible. | Negative. |
|---|-----------|-----------|-----------|
| 1. Fresh crude oil | 2 | 1 | 6 |
| 2. Fresh crude oil plus 0.1% aniline | 8 | Nil | 1 |
| 3. Crude oil weathered 2 years | 2 | 1 | 6 |
| 4. Crude oil refluxed over solid KOH | Nil | 2 | 7 |
| 5. Crude oil washed with acetic acid | Nil | Nil | 9 |
| 6. Crude oil refluxed 6 hours with Al-Hg | 2 | 6 | 1 |
| 7. Crude oil refluxed 18 hours with Al-Hg and then hydrolysed | Nil | 1 | 8 |
| 8. Crude oil plus 0.1% benzyl cyanide refluxed 6 hours with Al-Hg | 3 | 1 | 5 |
| 9. Crude oil plus 0.1% benzyl cyanide refluxed 18 hours with Al-Hg and hydrolysed | 4 | 3 | 2 |

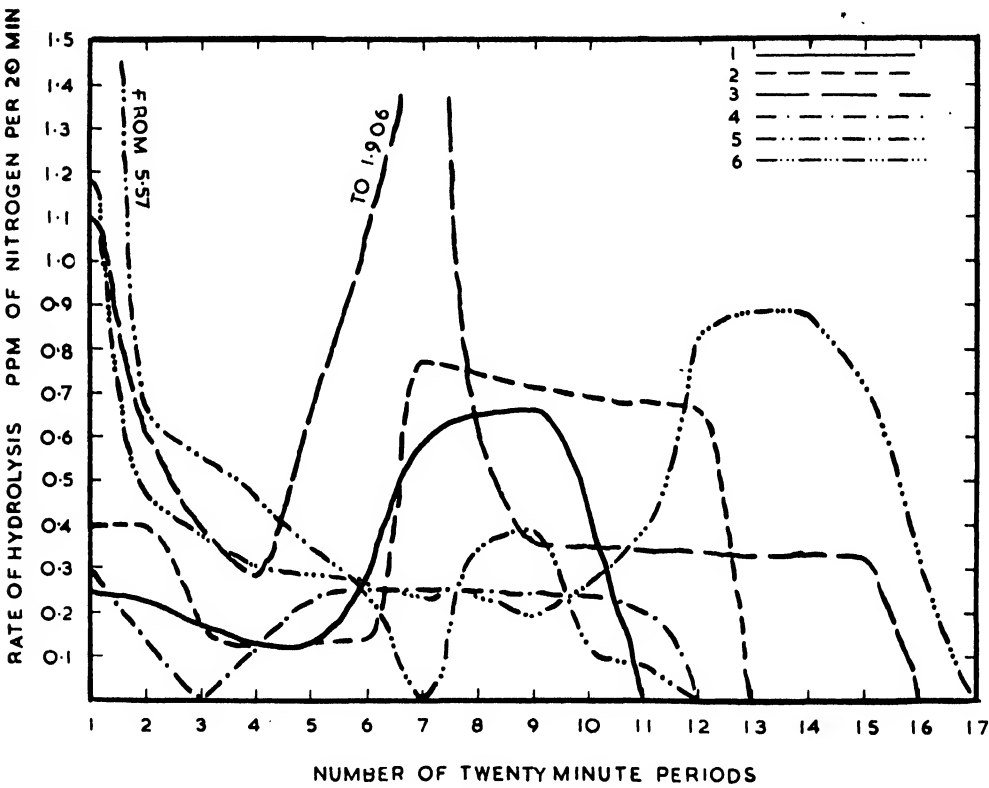


Fig. 1.

Fig. 1.—Rate of Hydrolysis of some Crude Shale Oils.
Sample No. 1. Acetic acid washed oil.
" No. 2. Acetic acid washed oil plus added benzyl cyanide.
" No. 3. Unwashed crude oil.
" No. 4. Unwashed crude oil after refluxing with Al-Hg for 20 hours.
" No. 5. Unwashed crude oil.
" No. 6. Weathered crude oil.

The aluminium amalgam reduction of the crude oil containing benzyl cyanide gave a definite increase in the primary amine content, which appeared to increase with time of refluxing.

RATE OF HYDROLYSIS OF CRUDE SHALE OIL.

Both amides and nitriles could exhibit most of the properties of the hydrolysable nitrogen components of the oil. A consideration of their properties suggested that it might be possible to distinguish between them by determining the rate of hydrolysis of the oil and of some amides and nitriles in solution in the oil, despite the small amount present.

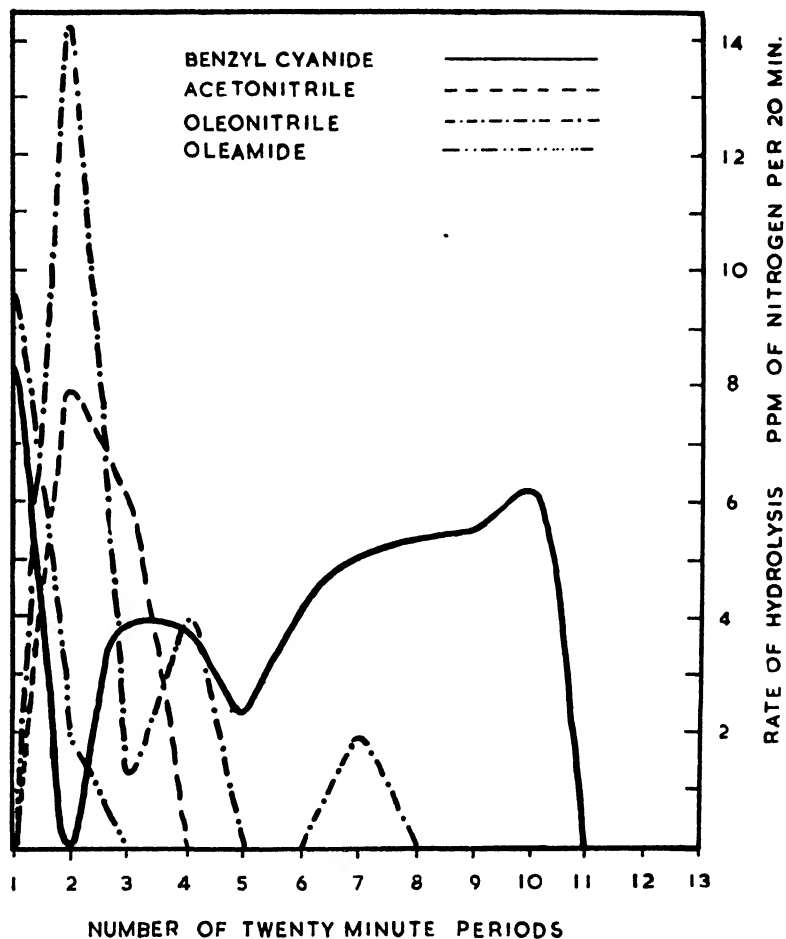


Fig. 2.

The results obtained with various samples of crude shale oil are presented graphically in Figure 1. With the samples of acid washed oil, the rate of ammonia evolution was not very high at first, and soon fell to a minimum which was followed by a pronounced peak or plateau in the rate curve. With the samples that had not been acid washed, the initial rate of ammonia evolution was much higher, but the peak or plateau was still observed in the latter part of the rate curve. This initially higher rate could be attributed to a combination of three factors: the possible presence of ammonium salts and the presence of

volatile tar bases in the crude shale oil together with the decomposition of some of the more readily hydrolysable compounds. All or part of these materials would be removed by the acid wash.

The results of the rate of hydrolysis of oleamide and some nitriles are presented graphically in Figure 2. The hydrolysis rate curves for the nitriles were of the same general type as those of the acid washed crude shale oil, by giving a pronounced minimum followed by a peak or plateau. Oleamide gave a rapidly decreasing rate curve without any indication of a subsequent peak.

Another inference drawn from this work was that the duration of the hydrolysis was a function of the amount of hydrolysable material present. This may be expected, as the rate of hydrolysis would be a function of the degree of contact between the oil and the caustic solution. Also, the rate of hydrolysis is obviously a function of the structure of the nitrile.

The significant difference in the hydrolysis rate curves for oleamide and for the nitriles suggests that the occurrence of a peak or plateau in the curve may be used as a tentative indication of the presence of nitriles in the oil. At present, no explanation can be given for the shape of the hydrolysis rate curve of the nitriles, though it appears that it may be due to the fact that the hydrolysis is a two-stage reaction in first giving rise to the amide. It is quite probable that some amides, as well as nitriles, may be present in the oil, but this method could not very well be employed to detect amides in the presence of nitriles.

FORMATION OF ORGANIC ACIDS ON HYDROLYSIS OF CRUDE SHALE OIL.

The results presented in Table VI show a fairly close correspondence between the amount of ammonia evolved on hydrolysis of the oil and the amount of organic acids formed at the same time. The discrepancies are relatively large, ranging from 20% to 50% of the amount of ammonia obtained, but the maximum difference was only 5.3 mg. of ammonia from 500 ml. of oil. Also, the necessarily involved method of isolation of the organic acids and the possibility of the presence of traces of esters in the crude oil, could tend to give high results, while any discrepancies in the determination of the ammonia would, if anything, tend to give low results. Since the acid obtained in each case was in excess of the ammonia liberated, the results can be interpreted with a reasonable degree of certainty as supporting the previous deduction that the hydrolysable nitrogen compounds present in crude shale oil are nitriles, and possibly some amides.

TABLE VI.

Organic Acids from the Hydrolysis of Crude Shale Oil.

(Results are expressed in mg. of ammonia as obtained from 500 ml. of acid washed oil.)

| Sample No. | Ammonia. | Organic Acids. |
|------------|----------|----------------|
| A | 7.9 | 13.2 |
| B | 10.4 | 12.3 |
| C | 10.7 | 13.2 |

SUMMARY.

From an examination of the effect of acid washing and of mild reduction on the hydrolysable nitrogen content of the crude shale oil, the rate of hydrolysis of the oil, and the determination of the amounts of organic acids formed by the hydrolysis of the oil, it appears that the hydrolysable nitrogen compounds

which are present in crude shale oil to the extent of 30-100 p.p.m. of nitrogen by weight are most probably nitriles. Traces of amides may also be present.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge with thanks the technical assistance of E. J. Wolanin and R. S. Hayes, and the permission granted by the management of National Oil Pty. Ltd. for the publication of this paper.

EXPERIMENTAL.

Determination of Hydrolysable Nitrogen.

A measured volume (generally 50 or 100 ml.) of crude shale oil and 150 ml. of 10% caustic soda solution was charged into a long-necked flask of 500 to 750 ml. capacity, and 5 ml. of commercial cresylic acid or amyl or butyl alcohol added. The flask was then fitted with a four pear fractionating column fitted to a condenser, the delivery from which dipped below the surface of 50 ml. of 2% boric acid in a dropping funnel. The funnel was sealed and fitted with a bunsen valve (Meneghini, 1945) to reduce the danger of an accidental "suck back". Heating was commenced, and maintained at a sufficiently low rate for the liquid to boil in the flask, but for very little to distil, the fractionating column acting as a dephlegmator at almost total reflux. After an hour the rate of heating was increased, so that approximately 100 ml. of water were distilled during the next half hour. After the distillation had been completed, the lower aqueous layer of the distillate was separated, and the oil distillate washed with 25 ml. of ammonia-free distilled water. This was added to the separated boric acid solution, which was then titrated with 0.05 N sulphuric acid, using screened methyl orange as indicator (I.P., 1946). This separation step was necessary, as otherwise the oil interfered with the titration by extracting the methyl orange from the aqueous phase.

Washing Crude Shale Oil with Glacial Acetic Acid.

In order to extract free ammonia and the tar bases from a sample of crude shale oil before using it for other work, it was necessary to acid wash it. The washing was carried out by mixing thoroughly the required amounts of oil and glacial acetic acid (which was soluble in the oil), and adding the required amount of water. The dilute acid layer was then separated, and the oil washed with a further amount of water.

Carbylamine Test on Crude Oil.

This test was carried out by boiling 10 ml. of the crude shale oil with 0.5 ml. of chloroform and 1.0 ml. of 10% caustic soda solution. All samples were prepared and, when cool, were submitted together to the "jury" for smelling.

Determination of the Rate of Hydrolysis of Crude Shale Oil.

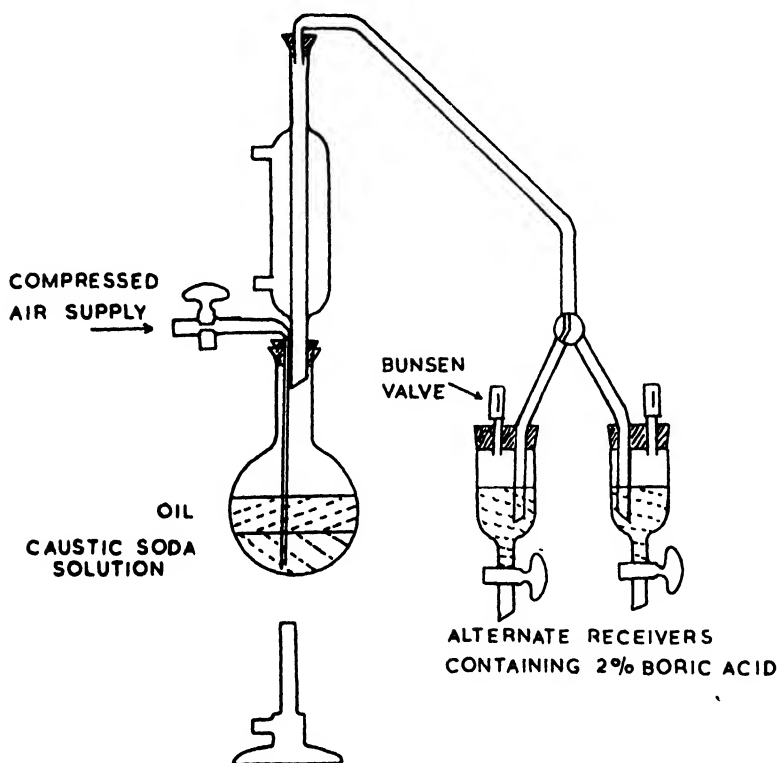
Crude shale oil (250 ml.), 10% caustic soda solution (300 ml.), and cresylic acid (10 ml.) were charged into a 750 ml. bolt-head flask fitted up as in Figure 3. The air flow was controlled so that three bubbles per second escaped through the boric acid solution in the receiver, and heating was commenced. The current of air served the dual purpose of carrying off the ammonia as it was liberated, and of mixing the oil and the caustic soda solution and eliminating bumping during the boiling. Zero time for the hydrolysis was taken as the time the mixture started to boil, as shown by the return of liquid condensate from the condenser. From that time, the air stream was diverted to alternate receivers containing boric acid, at 20 minute intervals. After the air had been diverted from a receiver, the aqueous layer was carefully separated from any oil that had distilled, and titrated with 0.05 N sulphuric acid, using screened methyl orange as the indicator. This process was repeated until at least three consecutive titrations indicated that no ammonia had been evolved during the period. The experiments were carried out in duplicate and the results averaged.

The rates of hydrolysis of the oleamide and the nitriles were determined by adding some of the compound to 250 ml. of the oil which had been completely hydrolysed. Equal amounts were added to each of two samples of oil, and the rates of hydrolysis of the two samples averaged.

Formation of Organic Acids on Hydrolysis of Crude Shale Oil.

A quantity of the crude shale oil to be tested was acid washed to remove ammonium salts and volatile tar bases, which could interfere with the analysis, and then washed several times with hot water to remove any residual traces of acid. The final washings were neutral to alkali blue.

Five hundred ml. of the washed oil were refluxed with 100 ml. of 10% caustic soda solution and 5 ml. of cresylic acid, in the same apparatus as used for the determination of the rate of hydrolysis, so that it was possible to determine when the hydrolysis was complete, as well as the total amount of ammonia evolved. The lower caustic soda layer was indistinguishable from the oil layer, except in bright sunlight or ultra-violet light, when the oil fluoresced a strong green.



APPARATUS FOR DETERMINATION OF RATE OF HYDROLYSIS OF OIL

Fig. 3.

The two layers were separated, and the oil washed with two 50 ml. portions of hot water. The combined caustic extract and washes were acidified with concentrated hydrochloric acid, and extracted with 100 ml. of gasoline. The gasoline was washed twice with 100 ml. portions of distilled water before the total (organic) acidity was determined by I.P. Method 1/46 (I.P. 1/46, 1948).

Before hydrolysis, the organic acid content of the crude oil was nil. A blank test indicated that the 5 ml. of cresylic acid added to act as an antifoaming agent during the hydrolysis contained organic acids equivalent to 0.73 mg. of ammonia. This was allowed for in calculating the amount of organic acids formed by the hydrolysis of the oil.

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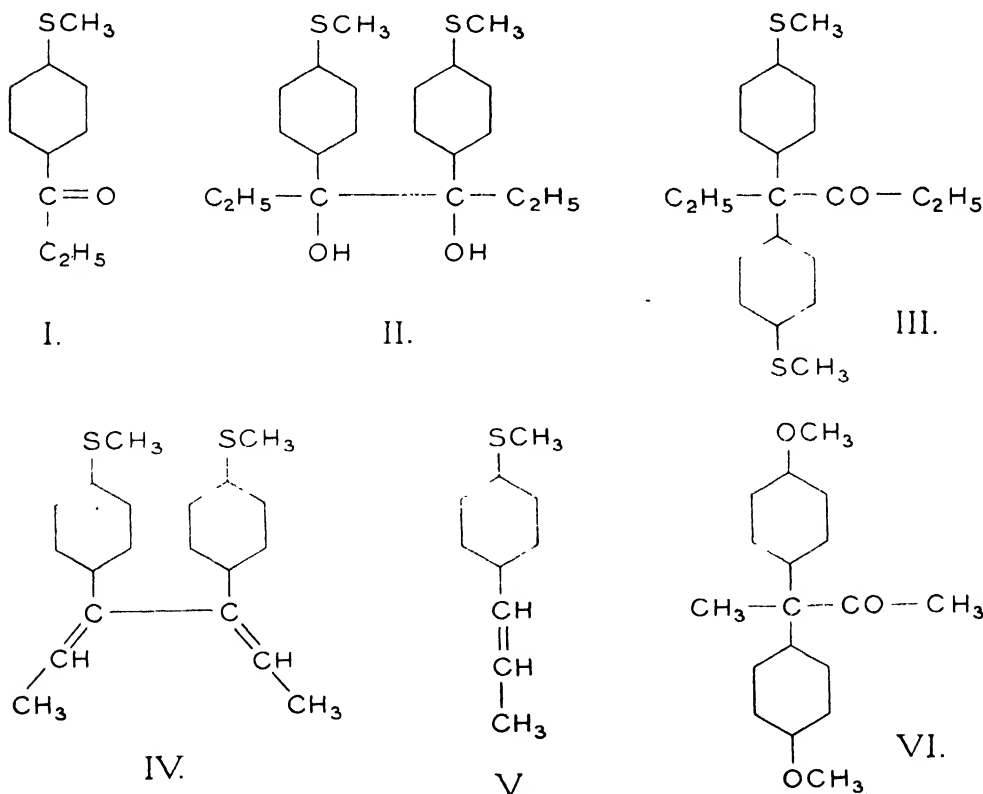
SYNTHETIC SEX HORMONES.

PART II. THE PINACOLS AND PINACOLONE OF *p*-METHYLMERCAPTOPROPIOPHENONE, AND THE PREPARATION OF DITHIODIENESTROL DIMETHYL ESTER.

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and E. O. P. THOMPSON.

Manuscript received, April 6, 1949. Read, June 1, 1949.

The successful dehydration of the pinacols from *p*-hydroxyacetophenone by Dodds, Goldberg, Lawson and Robinson (1939) to the corresponding butadiene, suggested the possibility of dehydrating the *pinacols*, II, derived from *p*-methylmercaptopropiophenone, I, to the sulphur analogue of dienestrol dimethyl ether IV. With potassium bisulphate or acetyl chloride, only the



pinacolone III was isolated. However, both the *meso* and *dl* forms of the pinacol gave with a mixture of acetic anhydride and acetyl chloride (cf. Dodds *et al.*, 1939), along with the pinacolone, a white crystalline solid which is the *hexadiene* IV.

Several methods of preparing the pinacols, II, were studied. Electrolytic reduction of the ketone, in an aqueous alcoholic solution containing potassium acetate, with a lead cathode as described by Price and Mueller (1944) gave a mixture of the pinacols which were separated readily owing to their different solubilities.

The high melting isomer is moderately soluble in hot benzene or alcohol and almost insoluble in ether, whereas the low melting pinacol is readily soluble in most organic solvents and can only be crystallized with difficulty from petroleum ether.

The method of Bachmann (1933) using sodium amalgam with alcohol in ether-benzene solution gave a good yield of the pinacols. With diaryl ketones this method gives a quantitative yield of the corresponding hydrol, the highly coloured sodium ketyl radicals being formed as intermediates. Possibly the reduction of *p*-methylmercaptopropiophenone proceeds by a different mechanism as no marked colour was developed. Magnesium and magnesium iodide which Gomberg and Bachmann (1927) introduced for the preparation of pinacols from diaryl ketones in quantitative yield (coloured iodomagnesium ketyl radicals being formed in the reaction) gave only small yields (8%) of the high melting pinacol, an olive green colour accompanying the reaction. However, Bachmann and Ferguson (1934) reported poor yields of pinacols from diaryl ketones containing alkoxyl groups with this reagent.

Aluminium amalgam and alcohol as used by Newman (1940) gave a fair yield of the pinacols.

Zinc dust and acetic acid used by Bachmann and Ferguson (1934) for the preparation of pinacols from diaryl ketones gave no detectable amounts of the pinacols but some thioanethole, V, was formed due to the easy dehydration of the hydrol as described by Hughes and Thompson (1948).

The pinacols were identified by oxidation with lead tetra-acetate as used by Price and Mueller (1944). The low melting pinacol was rapidly oxidized to the ketone, I, which was isolated quantitatively as the phenylhydrazone. The high melting isomer was oxidized slowly and using excess lead tetra-acetate the sulphoxide of *p*-methyl mercaptopropiophenone was isolated as its phenylhydrazone.

Attempts to identify the ketone, I, by selective oxidation with selenium dioxide followed by periodic acid, to *p*-methylmercaptobenzoic acid gave instead the sulphoxide of this acid. Mel'nikov (1935) had previously reported the oxidation of sulphides to sulphoxides and sulphones by selenium dioxide.

Attempts to esterify the high melting pinacol with acetic anhydride and pyridine, and by the Schotten Baumann method with benzoyl chloride, were unsuccessful, the pinacol being recovered unchanged.

Both pinacols were readily rearranged with acetic anhydride and sulphuric acid (Price and Mueller, 1944) and iodine and acetic acid (Gomberg and Bachmann, 1927); the latter method gave the better yield.

The pinacolone obtained would not give a dinitrophenylhydrazone or an oxime using the most stringent conditions of Bachmann and Barton (1938). This agrees with the observation of Sisido and Nozaki (1948) on the oxygen analogue.

Price and Mueller (1944) using the somewhat similar pinacolone 2:2'-di-(*p*-methoxyphenyl)-butan-3-one VI did obtain an oxime. Heating the pinacolone III, with hydroxylamine hydrochloride and alcohol in a sealed tube for six hours at 160° C. gave no oxime or rearranged product the pinacolone being recovered unchanged. Under similar conditions, Feith and Davies (1891) obtained *N*-acetyl-mesidine from acetomesitylene which under normal conditions will not form an oxime.

The structure of the pinacolone was assumed to be III, by analogy with the pinacolone obtained by Wessely, Kerschbaum, Kleedorfer, Prillinger and Zajic (1940). It gave a positive test for an enolizable hydrogen atom with *m*-dinitrobenzene and alkali in pyridine solution.

A 25% methyl alcohol solution of caustic potash did not split the pinacolone after eighty hours' refluxing.

This structure was confirmed by oxidation of the pinacolone or its sulphone with chromic acid to *p*:*p*'-dimethylsulphonylbenzophenone.

EXPERIMENTAL.

For the preparation of *p*-methylmercaptopropiophenone, see Hughes and Thompson (1948).

Electrolytic Reduction.

The apparatus consisted of a porous pot (fitted with a condenser) which contained the catholyte immersed in a 40% aqueous solution of potassium carbonate. The cathode was made of lead foil 100 sq. cm. in area, and the catholyte was a solution of *p*-methylmercaptopropiophenone (55 g.) in alcohol (125 ml.) to which water (50 ml.) containing potassium acetate (28 ml. saturated solution) was added. The electrolysis was carried out at reflux temperature using a current density of 0.02 amp./sq. cm., and after passing 120% theoretical current the mixture was poured into water.

The crude material was dissolved in hot alcohol, and on cooling the high melting pinacol separated and was completely removed by concentration of the mother liquors.

The crude high melting pinacol (10 g.) on repeated recrystallization from ethyl alcohol gave white crystals (8 g.) m.p. 168° C.

Found: C, 65.76; H, 7.19%. Calculated for $C_{20}H_{26}O_2S_2$: C, 66.23; H, 7.23%.

After removal of the alcohol from the mother liquors the residue was repeatedly recrystallized from petroleum ether (60–80°) to give the other pinacol m.p. 93° C.

Found: C, 66.00; H, 7.31. Calculated for $C_{20}H_{26}O_2S_2$: C, 66.23; H, 7.23%.

Reduction with Sodium Amalgam.

To the ketone (10 g.) dissolved in a mixture of anhydrous ether (70 ml.), benzene (70 ml.) and alcohol (7 ml.) was added sodium amalgam (167 g., 2%) and the mixture shaken in a tightly stoppered bottle for two hours.

No marked change in the initial yellow colour was noticed, and the solution gradually became cloudy as the high melting pinacol separated out.

The mixture was poured into water, acidified, and after separation of the organic layer extracted three times with hot benzene. The combined organic extracts were washed with water and the solvents removed under reduced pressure. The residue was mixed with ether and the insoluble pinacol (3.1 g.) filtered off. Evaporation of the ether followed by recrystallization from petroleum ether (60–80°) gave the other pinacol, m.p. 93° (3.9 g.).

The crude mixture of pinacols after removal of solvents may be rearranged with acetic acid and iodine to give the pinacolone (6 g.).

On the basis of yields obtained with pure pinacols this indicates at least 75% yield of pinacols.

Distillation of the crude pinacols under high vacuum gave no pinacol but a mixture of thioanethole V, ketone I and pinacolone III.

The pinacolone probably results from the effect of traces of acid and the ketone and thioanethole from disproportionation of the pinacols into ketone and hydrol, the latter being readily dehydrated.

Reduction with Aluminium Amalgam.

The ketone (30 g.) in absolute alcohol (300 ml.) and benzene (200 ml.) was treated with aluminium amalgam, prepared from previously etched foil (12 g.) and mercuric chloride (0.5 g.) and the mixture refluxed twenty-four hours. When poured into water and worked up in the manner described for the sodium amalgam method, the pinacols, m.p. 167° (10 g. crude) and m.p. 93° (8 g. crude) were obtained.

Reduction with Magnesium and Magnesium Iodide.

Magnesium iodide prepared by refluxing excess magnesium turnings (2.5 g.), iodine (7 g.) in a mixture of ether (18 ml.) and benzene (25 ml.) was shaken with the ketone (9 g.) in benzene (8 ml.). An olive green colour developed and after shaking three hours the liquid was decanted into water, acidified with hydrochloric acid and extracted with benzene. The organic extracts were washed with water and the solvents removed under diminished pressure. Ether was added to the oil and allowed to stand overnight, when a small amount of high melting pinacol (0.8 g.) separated. No pinacol could be obtained from the ether solution which consisted of unchanged ketone. Rearrangement of the residue after removal of the high melting pinacol gave oils from which no pinacolone could be crystallized.

Reduction with Zinc and Acetic Acid.

The ketone (10 g.) in glacial acetic acid (100 ml.) was treated with zinc dust (20 g.) during the course of two weeks of standing at room temperature. When the solution was decanted into water a semi-solid mixture was obtained which when filtered gave a solid, and an oil with a strong aniseed odour.

The solid was unchanged ketone identified by mixed melting point. The oil was distilled under reduced pressure to give thioanethole (2 g.) b.p. 143° at 25 mm. (approx.) and *p*-methylmercaptopropiophenone, b.p. 190° at 25 mm. (approx.).

Oxidation of the Pinacols with Lead Tetraacetate.

The low melting pinacol (1 g.) was suspended in glacial acetic acid (5 ml.) and the theoretical amount of lead tetraacetate (1.25 g.) was added. When both reactants had dissolved, the ketone was separated as the phenylhydrazone by addition of phenylhydrazine (1 ml.) in glacial acetic acid (3 ml.) and shaking thoroughly with the slow addition of water (2 ml.).

The phenylhydrazone after washing was recrystallized several times from alcohol, m.p. 84° . A mixed melting point with an authentic specimen prepared from *p*-methylmercaptopropiophenone showed no depression.

The derivative decomposed after several hours, and therefore was not analysed.

The high melting pinacol when treated in this way gave no phenylhydrazone unless excess lead tetra-acetate (2.5 g.) was used when a yellow compound was obtained m.p. 175° after several recrystallizations. It did not depress the melting point of an authentic specimen of the phenylhydrazone of the sulphoxide of the ketone.

The phenylhydrazones of the sulphoxide (m.p. 176°) and sulphone (m.p. 150°) of *p*-methylmercaptopropiophenone were prepared in the usual manner from the sulphoxide and sulphone and were recrystallized from alcohol.

Oxidation of p-Methylmercaptopropiophenone with Selenium Dioxide and Periodic Acid.

The ketone (10 g.), selenium dioxide (12.5 g.) and dioxane (60 ml.) were refluxed four hours during which black selenium separated. The solution was decanted and the excess dioxane removed under reduced pressure. The residue was extracted with ether, the ether removed, water (50 ml.), potassium periodate (12.8 g.) and concentrated sulphuric acid (1.5 ml.) added and the mixture shaken and stood overnight. The solid material was filtered off, treated with caustic soda and filtered. The filtrate was acidified and the residue recrystallized from water to give a pale yellow solid (2.2 g.) m.p. 229° , which did not depress the melting point of an authentic specimen of *p*-carboxyphenyl methyl sulphoxide.

The sulphoxide m.pt. 233° and sulphone m.pt. 267° of *p*-methylmercaptobenzoic acid were prepared from the acid by oxidation in the usual way, in acetone and acetic acid solution respectively, with hydrogen peroxide (30%). They both recrystallized from water in white crystals.

Found : C, 51.17 ; H, 4.50 ; S, 17.25%. Calculated for $C_8H_8O_3S$: C, 52.12 ; H, 4.38 ; S, 17.4%.

Found : C, 47.26 ; H, 3.94 ; S, 15.75%. Calculated for $C_8H_8O_4S$: C, 47.96 ; H, 4.03 ; S, 16.02%.

Pinacolone Rearrangement.

The pinacol (10 g.) was suspended in acetic anhydride (50 ml.) and concentrated sulphuric acid (1.25 ml.) added drop by drop. A purple colour was obtained which faded to a light brown and all the solid dissolved. The solution was poured into water and neutralized with sodium carbonate when the oil obtained gradually solidified.

The solid was recrystallized from alcohol to give 2 : 2-di-(*p*-methylmercaptophenyl)-hexane-3-one m.p. 90–95°.

Concentration of the mother liquors gave a small amount (0.2 g.) of white solid m.p. 150°. Further concentration gave more pinacolone VI. The pinacolone fractions on repeated recrystallization from alcohol had m.p. 95° C.

Found : C, 69.4 ; H, 6.90%. Calculated for $C_{20}H_{24}OS_2$: C, 69.69 ; H, 7.02%.

The small amount of impurity on recrystallization had m.p. 157°.

Found : C, 65.3 ; H, 6.8%. This was possibly the isomeric pinacolone.

The yield was slightly better, 70%, with the high melting pinacol, the other isomer giving 60% yield.

Alternatively the pinacol (5 g.) was refluxed with acetic acid (25 ml.) and a crystal of iodine for several hours and then poured into water and neutralized. When recrystallized both pinacols gave the pinacolone (3.8 g.) m.p. 95° C. No other product was isolated in this case.

Oxidation of the Pinacolone.

Potassium Permanganate. Formation of the Sulphone. The pinacolone (1 g.) in glacial acetic acid solution was treated slowly with a solution of potassium permanganate (1.37 g.) in water (40 ml.). After addition was complete the solution was decolorized by sulphur dioxide. A white precipitate remained which when recrystallized from methanol gave the sulphone (0.68 g.) m.p. 149.5° C.

Found : C, 57.8 ; H, 6.05 ; S, 15.36%. Calculated for $C_{20}H_{24}O_3S_2$: C, 58.8 ; H, 5.92 ; S, 15.7%.

The sulphone was also obtained by oxidation with hydrogen peroxide solution (30%) in acetic acid solution at 100° C.

Chromic Acid. The pinacolone (1.15 g.) or sulphone (2 g.) was dissolved in glacial acetic acid and chromic acid crystals (2 g.) together with concentrated sulphuric acid (1.3 ml.) added and the mixture refluxed for thirty minutes. The reaction mixture was poured into water and almost neutralized with sodium carbonate. A solid separated which was filtered off, washed with water and recrystallized from water, m.p. 236–237° C.

The compound was *p* : *p*-dimethylsulphonyl-benzophenone.

Found : C, 53.0 ; H, 4.23 ; S, 18.56%. Calculated for $C_{18}H_{14}O_3S_2$: C, 53.2 ; H, 4.17 ; S, 19.0%.

Dithiodienestrol Dimethyl Ether. The pinacol (5 g.) was refluxed with acetyl chloride (6 ml.) and acetic anhydride (9 ml.) for thirty minutes and poured on to ice. The semi-solid material recrystallized from alcohol to give a mixture of pinacolone and diene (3 g.) m.p. 80° C. When taken up in alcohol and cooled slowly the hexadiene (0.7 g.) m.p. 125–133° crystallized out and was carefully filtered off, the pinacolone (2 g.) m.p. 85–93° crystallizing in the receiver.

Repeated recrystallization of both fractions gave the pinacolone (1.3 g.) m.p. 95° C., and the dithiodienestrol dimethyl ether (0.4 g.) m.p. 141°.

Found : C, 72.8 ; H, 6.87 ; S, 19.76%. Calculated for $C_{20}H_{22}S_2$: C, 73.6 ; H, 6.75 ; S, 19.6%.

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METALLOGENETIC EPOCHS AND ORE REGIONS IN THE COMMONWEALTH OF AUSTRALIA.*

By W. R. BROWNE, D.Sc.

With one Table and six Text-figures.

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INTRODUCTION.

The wise old Hebrew prophet well knew the value of the inspiration and encouragement to be got from a contemplation of the illustrious past when he counselled his countrymen: "Look ye unto the rock whence ye are hewn, and the hole of the pit whence ye are digged; look unto Abraham your father and to Sarah that bare you." It was doubtless with the same thought in mind that the Royal Society of New South Wales ordained that the memory of that great citizen and scientist, Rev. W. B. Clarke, who may be regarded as its second founder, should be kept green by the delivery of an annual lecture dedicated to his name. I am very proud and honoured to have been asked by the Council to be the lecturer for this year, for I have long been an ardent admirer of the "father of Australian geology", of his geological enthusiasm, scientific insight, tireless energy, single-minded devotion to duty and uncompromising championship of what he was convinced was right. The pioneer geological work that he accomplished in the face of many obstacles must ever be an inspiring influence to geologists in this country.

Like his successors, David and Andrews, in the same field of investigation, Clarke combined an ardent love of geology for its own sake with a strong determination to apply his knowledge for the material advancement of his country. The implied recognition of the twofold character of geology is apt to be obscured alike by those who think of it simply and solely as a means to material gains and by those rare souls whose thoughts never stray from the pursuit of the so-called academic aspects of their studies. Only in so far as it holds a proper

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balance between the cultural and the utilitarian can geological science in this country hope to command the respect and attention that it merits and make the progress that it should.

For my lecture to-night I have chosen a theme which, while strictly speaking in the realm of pure geology, yet should hold some interest for the economic geologist, since the study of ore-deposits stands to gain from every attempt to arrange our knowledge in orderly fashion. From time to time there have been papers written and addresses given on the questions of metallogenetic epochs and ore provinces in various parts of the Commonwealth and in the continent as a whole. One thinks particularly of papers by E. S. Simpson and E. C. Andrews, by Waterhouse, Stillwell and Ball, and of the more recent work of E. S. Hills and Austin Edwards and the presidential addresses of Jones in Queensland and Prider in Western Australia.* While deriving much from all this earlier work, my present intention is chiefly to analyse our information about the ore-deposits of Australia in the setting provided by an increased knowledge of the epochs of tectonic and igneous activity. The result must be regarded merely as a progress report and an interpretation, some part of which is bound later to be rejected and some to be modified.

If we were to consider ore-deposits in a very comprehensive way so as to include those of detrital or otherwise derivative character, we could recognise an almost endless succession of ore epochs, which would include the time of deposition of the very important pre-Cambrian sedimentary iron ores of Western Australia and South Australia, the Tertiary periods during which our laterites and bauxites and our alluvial gold and tin deposits were formed, and the Quaternary epochs marked by the concentration of the very valuable zircon and rutile deposits at various places along the coast of eastern Australia and Tasmania. We shall, however, confine our attention to the primary ore-deposits, that is to say, those deposits of ores which are related to the igneous rocks.

GEOGRAPHICAL DISTRIBUTION OF ORE-DEPOSITS.

Australia may be broadly divided into three great topographic regions (Fig. 1): (a) the Great Western Plateau, including the pre-Cambrian shield and stretching over Western Australia, the greater part of Northern Territory and much of South Australia, with extensions into the far west of Queensland and New South Wales; (b) the Central-Eastern Lowlands, made up largely of the Mesozoic sediments of the Great Australian Artesian Basin and the Cainozoic deposits of the Murravian Basin; and (c) the Eastern Highlands belt, composed mainly of Palæozoic rocks and occupying much of eastern Queensland and New South Wales, the greater part of Victoria and virtually all of Tasmania.

The primary ore-deposits are confined to the first and third regions, wherein the rocks have been folded again and again and invaded by igneous magmas, most of which were ore-carriers. The strata of the second region are level-bedded, and their deposition has been unaccompanied by volcanic activity on a large scale. There are also in the plateau regions marginal areas of barren, horizontal or gently folded strata, such as the Desert Basin and the North-West and South-West Basins in Western Australia, the Nullarbor Plain, the areas occupied by Mesozoic rocks in all the States and the great Sandridge Deserts. Some of these form lowlands and some highlands, and on the other hand there are lowlands, particularly in the coastal belts, composed of intensely folded ore-bearing rocks. Nevertheless, broadly speaking, the highland and lowland divisions of Australia have not merely a tectonic and structural but also a considerable economic import.

* See list of references.

The precise conditions of deposition of the Older pre-Cambrian rocks of the Great Western Shield we do not know ; but the Upper pre-Cambrian and Cambrian rocks were laid down in a great median basin of deposition including at least two elongated troughs, one running north and south in South Australia, the other east and west in Central Australia, partly on the site of the Macdonnell Ranges. In the first trough sediments to a maximum thickness of 12 or 15 miles were deposited before it was extinguished by folding of its strata. The Eastern Highlands belt was the site of the great Tasman Geosyncline, wherein sinking and deposition alternated with folding and plutonic injection throughout Palæozoic and Mesozoic time. The geosynclinal strata—chiefly marine—and their associated volcanic rocks became hosts for the metalliferous ores brought in contemporaneously with volcanic activity or introduced with the formation of plutonic bathyliths during the orogenic epochs.

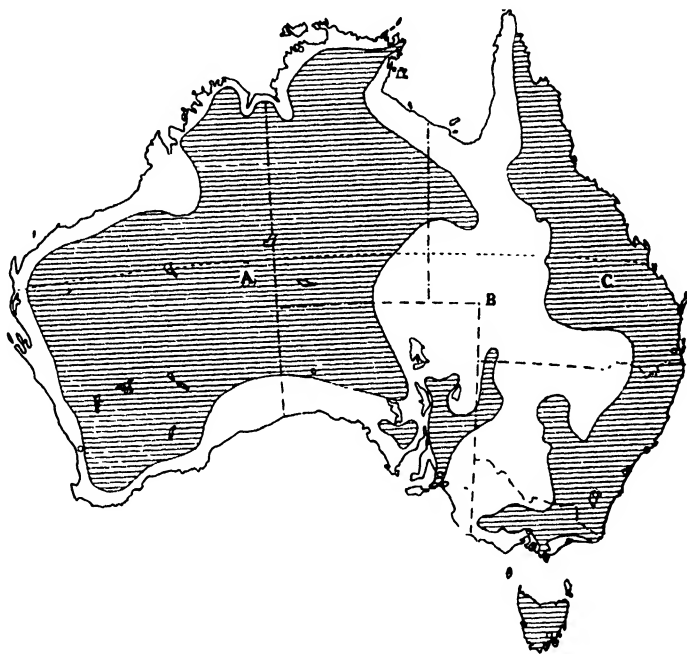


Fig. 1.—Topographic Regions of Australia.

- (a) The Great Western Plateau.
- (b) The Central-Eastern Lowlands.
- (c) The Eastern Highlands Belt.

The blanketing effects of the unfolded post-Palæozoic beds are such that any ore-deposits in the underlying pre-Cambrian and Palæozoic rocks are hidden away as securely as if they did not exist. There is little doubt that ores are present in these old foundation-rocks, but they are at an extreme depth of at least 7000 feet in south-eastern Queensland and more than 5000 feet in the Murravian Basin. There is some reason to believe that the Cretaceous rocks of the Great Artesian Basin once encroached upon the highlands farther than at present, and that the rich ore-deposits of, for instance, Cloncurry in Queensland and Broken Hill and Cobar in New South Wales, have been revealed to us through erosion of the sediments of the Cretaceous epicontinental sea that covered the site of the Great Artesian Basin. Even in known ore-bearing areas a few inches of sand and soil can most effectively conceal the presence of metalliferous rocks,

but nowadays some of the hidden deposits are being detected by geophysical and geochemical prospecting.

RELATION OF ORES TO IGNEOUS ROCKS.

Geologists are not unanimous as to the exact origin and mode of emplacement of ores of the economic metals, but it is a matter of general agreement that they are somehow genetically related to magmas or igneous emanations which ascend from the deeper layers of the earth's crust and come to rest at depth or are ejected on to the surface. The question whether the ore-minerals were original and essential constituents of the magma, or were present in the invaded rocks, ingested by the ascending fluids and later regurgitated, as it were, does not greatly concern us; neither need we discuss the much debated problem of the origin of granite, with which so many ore-deposits are connected. All we are considering at the moment is the association of ore-deposition with the formation of igneous rocks at different geological epochs, which is far too common and widespread a phenomenon to be of other than genetic significance.

Some of our primary ores are in close and apparently genetic relation to volcanic lavas. For instance, masses of native copper were found in andesite of Devonian age in the Keelbottom River (Queensland), and there is reason to suppose that ore-mineral and host-rock are related. The small deposits of native copper in amygdalae in the Permian trachybasalts on the South Coast of New South Wales are clearly comagmatic with the lavas, though doubtless the result of decomposition of cupriferous ferromagnesian minerals by deuteric solutions and subsequent deposition. It has been suggested that the silver-lead ores of Narlarla in West Kimberley (W.A.) are related to neighbouring volcanic plugs of Tertiary leucitic rock, and the quartz-veins containing gold, silver-lead and copper among the Upper pre-Cambrian Nullagine beds in the Pilbara district of Western Australia are considered to be comagmatic with the contemporaneous acid and basic lavas, while the gold of Cracow (Queensland) is thought by Denmead to have been introduced by andesitic magma in Mesozoic time.

The presence of ore-deposits in lavas may, however, be purely fortuitous, and it is probably so where gold is found in the Cambrian lavas or "diabases" of Heathcote (Victoria) and in the sheared Silurian andesites of Forbes, Blayney and Lucknow (N.S.W.).

Association of ores with hypabyssal intrusions, though far from common, is not unknown. In Western Australia there are many deposits of copper, lead, zinc and silver connected with basic dykes which have been variously assigned a late pre-Cambrian and a Palæozoic age but which may in fact belong to a number of different epochs. The copper of Blinman in the Flinders Ranges and other places in South Australia may have been introduced with certain basic dykes and other minor intrusions of Cambrian age. At Walhalla in central-eastern Victoria gold is closely associated with a swarm of dykes whose compositions range from intermediate to ultrabasic. On a much smaller and purely uneconomic scale are the auriferous pyrites of Mesozoic (?) quartz-dolerites and the gold associated with Tertiary (?) syenite-porphyrries in Tasmania. The copper and gold deposits of Cobar (N.S.W.) seem to be proximately related to intrusions of quartz-porphyry, but these are in their turn probably comagmatic with the granites cropping out at a distance of about 25 miles from the town.

It is clear that as with the volcanic rocks it may be hard to establish the existence of a genetic relation between ores and hypabyssal intrusions, since the jointing, cracking and shearing or faulting to which such rocks are liable may provide channels for ore-solutions not directly or at all connected with them.

By far the largest proportion of ore-deposits in the Commonwealth appear to be related to plutonic intrusions. They may be direct crystallizations or segregations of early-formed minerals, such as the chromite, platinum and osmiridium of the ultrabasic rocks, but for the most part they are of late deposition, crystallized in late differentiates or from late-magmatic or post-magmatic solutions, and chiefly in association with acid and intermediate rock-types. It is difficult to relate specific ore-minerals to specific rocks, but there is some evidence in the Commonwealth suggesting that gold accompanies granodiorite and copper and iron quartz-monzonite, while tin, tungsten, molybdenum, bismuth and antimony ores are of course found in general with the most acid types of granite. On the other hand examples have been reported of a zonal arrangement of ores around the margin of a bathylith according to the temperatures of formation, as at Heemskirk and other places in Tasmania and at Wolfram Hill in North Australia. In such circumstances the dominance of a particular metal in the ore-deposit is largely a function of the depth of erosion of the *terrain* or the distance from the edge of the intrusion.

The contention has been put forward that it is not necessarily correct to assume that a given primary ore-deposit is related to a neighbouring plutonic intrusion where the two are not in visible connexion. But around many bathyliths the normal contact-areole may have a surface-width of as much as a mile or more, and the deposition of relatively low-temperature ore-minerals from mobile magmatic solutions under pressure could surely have extended far beyond this limit. In any case the visible boundaries of its outcrop are not necessarily indicative of the underground extension of a bathylith, and the occasional presence of felspar and tourmaline in ore-bearing quartz-veins sufficiently attests their magmatic origin even when they cannot be traced into pegmatites.

Ores are seldom monometallic, and complex types are known in which quite a number of metals are of approximately equal importance, but it is probably true that in the majority of instances one or a few metals are dominant or predominant.

EPOCHS OF IGNEOUS ACTIVITY AND METALLOGENESIS.

From the close connexion between ore-deposition and plutonic invasion it naturally follows that the great epochs of folding and plutonic invasion were also metallogenetic epochs. The bathyliths belong, broadly speaking, to two types, the synchronous or syntectonic and the subsequent or epitectonic. Opinions are divided as to the mode of emplacement of these, but the view is widely held that the first were formed largely through a process of transformation *in situ* of original sedimentary rocks by granitizing fluids, and that those of the second type represent the consolidation of bodies of liquid magma. However that may be, in the Commonwealth the synchronous type of bathylith was characteristic of the earliest known pre-Cambrian diastrophism, and of the late Ordovician and late Silurian orogenic epochs in eastern Australia. In general the other bathyliths are of subsequent type, though it would appear that some of those of late Middle pre-Cambrian age are synchronous. With both types ore-deposits are found to be associated.

Other possible metallogenetic epochs coincide with the times of injection of minor intrusions or with episodes of vulcanism, but, as already pointed out, these were not very important in Australia, and it can be said that with the vast majority of lava-flows and minor intrusions there have been found no signs of ore-deposits whatever. On the other hand the ores whose connexion with plutonic intrusions—bathyliths or stocks—is reasonably certain are legion.

All the forms of igneous activity referred to are related to geosynclinal deposition and deformation, but the volcanic and the hypabyssal may also be quite independent of it and be purely terrestrial in character.

In the geological record of the Commonwealth it is possible to discern nine epochs of folding and bathylithic formation accompanied by ore-deposition (see Table), and in addition a few epochs of hypabyssal intrusion and volcanic activity to which some ore-formation may be attributed.

Pre-Cambrian.

Probably for the world as a whole, as for Australia, the pre-Cambrian ores loom much larger than the sum total of all those of subsequent geological time. This may indicate, of course, that the pre-Cambrian was specially characterized by the introduction of ore-minerals, but it must be remembered that it embraced more than two-thirds of known geological time, and that it may have comprised several periods of deposition followed by epochs of folding and bathylithic injection, and punctuated by intervals of erosion sufficiently long to permit the complete elimination of all traces of the sediments. Professor Arthur Holmes has demonstrated by Pb/U determinations that at least seven distinct epochs of bathylithic injection and (presumably) orogenesis may be recognised for the pre-Cambrian. At present in the Commonwealth we have evidence of only three main periods of deposition and two main epochs of diastrophism and injection. The first or Pilbaran diastrophic epoch closed what we may call the Lower and the second or Houghtonian the Middle pre-Cambrian sedimentation. Probably the earliest metallogenetic epoch of which we have knowledge is that to which the gold ores of Kalgoorlie (W.A.) belong. There has been much controversy about the circumstances in which these ores were introduced, some workers relating them to the intrusions of the Younger Greenstones (dolerites) through their acid differentiates, a series of sodic porphyries and porphyrites, others preferring to connect them with hidden intrusions of granite similar to those occurring, with an accompaniment of auriferous quartz-veins, a few miles away. If the first view is correct, and it seems to have a good deal of justification, the epoch of metallization is probably Pilbaran, for the injection of the greenstones as sill-like masses seems to have heralded the Pilbaran folding, and indeed the rocks of the Younger Greenstone suite may be comagmatic with the granite-gneisses that were formed during the Pilbaran epoch. If on the other hand the gold is related to a granite, then its introduction most probably belongs to the Houghtonian epoch.

So far as we know, comparatively few ore-deposits are related to the Pilbaran intrusions. Apart from Kalgoorlie and a few other fields, such as Meekatharra and Wiluna, in which the gold ores are in greenstones and similar to those of Kalgoorlie, the only other known deposits which we can well assign to the Pilbaran epoch are the chromite contained in ultrabasic greenstones at Coobina in the north-west of Western Australia and the platinum which is present in rather insignificant amounts in certain altered basic or ultrabasic intrusions belonging to the Older Series in the Barrier Ranges near Broken Hill, New South Wales.

For Western Australia the Pilbaran and the Houghtonian were by far the most important epochs of ore-formation. During the second a great series of granitic bathyliths and stock-like masses were injected, with potassic and sodic pegmatites, and to them are related most of the gold occurrences of the State, together with a number of other ores, chiefly those of tin, iron, tungsten, molybdenum, tantalum and niobium, and minerals containing uranium, beryllium, lithium and the rare earths.

To the Houghtonian epoch also are assignable many ore-deposits outside Western Australia. In North Australia the gold of Buldiva, Pine Creek and a

number of other fields, the tin of Maranboy, the tantalum of Rum Jungle and the copper of Yeuralba all appear to be related to Houghtonian granites. Coming farther south we note that the gold of Tanami and The Granites and the auriferous hæmatite lenses of Tennant Creek are of the same age. At Hatches Creek are tungsten deposits, and in the Macdonnell Ranges the Oolgarra granites brought in the gold of the Winnecke, Arltunga and other fields, while the associated pegmatites have yielded beryl. Recently uranium has been reported from Hart's Range in the Eastern Macdonnells.

The chief primary ores of pre-Cambrian age in South Australia are the copper deposits of Wallaroo and Moonta, whose parent magma appears to have been that which produced the Houghtonian granites and pegmatites with which they are associated. A little uranium is associated with the copper ores. The uranium ores of Mt. Painter, in the extreme north of the Flinders Ranges, are in granitic igneous intrusions, but whether these are of Houghtonian age or later is still in dispute, as is likewise the age of the granites in the east of the State with which the radio-active ilmenite of Olary is associated. Traces of uranium minerals have also been noted in Houghtonian (?) pegmatites in Eyre Peninsula. Apart from rutile and monazite which are found in titaniferous pegmatites in a few places, there do not appear to be any further pre-Cambrian ores of note in South Australia.

Across the border the great silver-lead-zinc deposit of Broken Hill, with copper, gold, cadmium and other minor constituents, is most reasonably regarded as comagmatic with Houghtonian granites like those of Mundi Mundi, and farther to the north in the Barrier Ranges are pegmatites with tinstone, wolfram and amblygonite. The other easterly projection of the Great Western Plateau contains the copper and iron deposits of the Cloncurry region including those of the Cloncurry district, Mt. Philp, Mt. Oxide and a number of other outlying fields, together with the silver-lead and copper lodes of Mt. Isa. All these appear to be related to the Cloncurry and Templeton River granites. Much farther north the silver-lead of Lawn Hill is probably in part of the same age but perhaps partly younger. Rutile, beryl, monazite and other rare minerals occur in pegmatites west of Mt. Isa, related to the Templeton River granite. East of Cloncurry the pre-Cambrian disappear under Mesozoic beds, to emerge in the Etheridge and other goldfields, where some of the gold at all events seems to be pre-Cambrian and probably Houghtonian.

The possibility that some of the gold, silver-lead and copper of Western Australia, and particularly of the Pilbara area, is related to contemporaneous lavas of Nullagine (Upper pre-Cambrian) age and basic dykes of latest pre-Cambrian has already been referred to. The presence of these ores may be regarded as marking a minor pre-Cambrian metallogenetic epoch in Western Australia.

Cambrian.

Upper pre-Cambrian seems to have passed into Palæozoic time without any orogenic break, and sedimentation continued till the end of the Middle Cambrian epoch. Most of it occurred in the great Central Basin, which included the sites of the Mt. Lofty and Flinders Ranges in South Australia and extended east into New South Wales and Queensland, and south and south-east to Victoria and Tasmania. In the north it embraced much of Northern Territory (including the Macdonnell Ranges) and spread into East Kimberley. At this time also the Tasman geosyncline was probably initiated in eastern Australia. During the Tyennan epoch, shortly after the close of the Middle Cambrian, Upper pre-Cambrian and Cambrian rocks were folded together, and there was injection of granites, pegmatites and quartz-veins along the southern and eastern Mt. Lofty Ranges and to the south-east into the far west of Victoria. The intrusions

seem to have extended north to the north-east of the Macdonnell Ranges, and granite was injected into the Upper pre-Cambrian rocks in the far north-west of New South Wales, in the Koonenberry, Wertago and Nuntherungie Ranges and at Tibooburra. At the same time granites, granite-porphyrries and syenites invaded the Lower and Middle Cambrian and Upper pre-Cambrian rocks of northern and western Tasmania at Middlesex Plains, Mt. Darwin and elsewhere.

These irruptions of magma were responsible for a limited amount of ore-deposition. They probably brought in the copper of the Mt. Lofty and Flinders Ranges fields, as at Burra, Kapunda, Balhannah, Callington, Blinman and Yudnamutana, and the gold of Mt. Grainger and other goldfields. The copper, however, may in part have come in with minor basic intrusions that intersect the Cambrian and Upper pre-Cambrian rocks. It has been argued that the magmas responsible for the radio-active ores of Mt. Painter and Olary invaded Upper pre-Cambrian rocks, and if so they are probably Tyennan. Some beryl-bearing pegmatites in the eastern Mt. Lofty Ranges may be of the same age, and so may the tungsten of Wauchope Creek in Central Australia.

In the far north-west of New South Wales the granites introduced copper and gold, and it may be that some of the Lawn Hill silver-lead ores of North Queensland, which are in gently folded Cambrian rocks, were emplaced during the same epoch.

Mineralization related to the Tyennan granites of Tasmania was not important or extensive; in fact only some copper and the iron-ores of the Jukes-Darwin field have been referred, and with some doubt, to their entry. If, however, as has been suggested, the ultrabasic intrusions of western Tasmania are Cambrian, then chromium, nickel and osmiridium minerals are to be added to the Tyennan ores.

On the whole this metallogenetic epoch was far from spectacular, except in South Australia, where more copper has been mined than in any other State.

Ordovician.

After the Cambrian period by far the most important metallogenetic events in the geological history of the Commonwealth occurred in eastern Australia, which was the site of the Tasman geosyncline. At the close of the Ordovician sedimentation came the Benambran epoch of folding and formation of synchronous bathyliths of somewhat acid granites with pegmatites. Diastrophism affected a broad median zone running through eastern Victoria and the highlands and Western Slopes of New South Wales, which must have been prolonged into Queensland. Two chief belts of granitic bathyliths are known, the more westerly of which, about 100 miles wide, starts in the highlands of eastern Victoria, passes through Albury and the Upper Murray country, to the east of Wagga, and north through Junee as far at least as a point 20 miles west of Condobolin. Some gold and tin in Victoria and in south-eastern New South Wales seems to have been introduced with the granite and pegmatites, and gold further north at Junee Reefs and Sebastopol, but this region was subjected to at least three subsequent epochs of folding and plutonic invasion, and it is by no means easy to determine beyond doubt the respective ages of all the ore-deposits. It is possible that some of the tin-ores of the Western Slopes, as at Mt. Tallebung, Buddigower and elsewhere, are Ordovician, but information on the point is lacking.

Silurian.

At the end of the Silurian Period during the Bowring epoch the geosyncline suffered further diastrophism except for a narrow zone in the extreme west. Synchronous bathyliths and porphyry lenses associated with the folding are widespread in the Eastern Highlands and Western Slopes of New South Wales

and extend into eastern Victoria. We find them in New England east of Armidale and south as far as Walcha, in the Central Highlands at Cow Flat and elsewhere south of Bathurst, at Crookwell and Wheeo north of Goulburn and probably also as far west as Nymagee. They are also seen at Breadalbane and Gunning, east and west of Lake George, about Adelong and Batlow, near Grenfell, in the Australian Capital Territory and south to Cooma, on the Kosciusko plateau, near Delegate, north of Albury and across the border into Victoria to the Omeo district. Many of the rocks are hybridized and of the composition of quartz-diorites. Gold seems to be genetically related to many of the gneissic granites and porphyries in Victoria and in New South Wales, as at Adelong, Cooma, Michelago, Tuena, Wyalong and perhaps too at Hillgrove (New England). Copper is known from Cow Flat, iron ore occurs at Breadalbane west of Goulburn, and a series of small deposits of iron and copper ores borders the Murrumbidgee batholith on its eastern side from the Cotter junction south to Cooma.

To the Bowning epoch are usually assigned the sheets of ultrabasic intrusives and serpentinized peridotites, pyroxenites, etc., which form two long sub-meridional belts on the South-Western Slopes, one running through Gundagai and the other to the east of it. A certain amount of gold has been yielded by these intrusions, but it is very doubtful if they are more than host-rocks, though they may have been comagmatic with granites and porphyries which were the probable ore-carriers. Chromite has been got from the ultrabasic rocks at several places. The platiniferous serpentine of Fifield is also possibly late Silurian.

No ore-deposits of late Silurian age have been definitely recognised in Queensland, though it is by no means unlikely that such exist. They may, of course, be largely hidden beneath the sediments of the Great Australian Artesian Basin.

Middle Devonian.

Tasmania and central Victoria escaped the Bowning orogeny, and Silurian and Devonian rocks there were deformed together during the Tabberabberan orogeny that brought the Middle Devonian epoch to an end. The belt of folding must have continued north into New South Wales, where we find a number of plutonic masses intrusive into Silurian and overlain by Upper Devonian rocks, which seem to belong to this epoch. They are of granite and/or granodiorite, and of subsequent type, and apart from field-relations there is no certain way of distinguishing between them and the Carboniferous intrusions, which resemble them petrologically and whose region of intrusion overlapped theirs.

No intrusions of this age are certainly known in Queensland, though the belt of folding must have extended into that State. The gold-bearing granites of Charters Towers were thought by Jack to be overlain farther north by Upper Devonian beds, and if so the gold of this field and of Ravenswood and other adjoining fields may be Middle Devonian. In New South Wales Andrews recorded from east of Parkes a granite which must be Tabberabberan, and not improbably it or an allied intrusion was responsible for the mineralization of the Forbes-Parkes area, in which the auriferous solutions took advantage of shear-zones in the Silurian sediments and contemporaneous andesitic flows. It may be with a granite of the same age that the wolfram of Yeoval is connected. In the Cobar-Nymagee-Mt. Hope area there are massive granites and porphyries locally crushed, which are probably comagmatic, intrusive into Silurian and overlain by Upper Devonian beds and therefore Tabberabberan. Their magma is most likely to have been the vehicle for the gold, copper and other ores of the region.

A composite bathylith of granite and granodiorite with marginal quartz-porphyrries and quartz-porphyrtes stretches north for some 50 miles from Bungonia near Goulburn to Wombeyan and beyond. There is but little mineralization known to be connected with it, but the silver-lead ores of the old Carrington mine near Marulan may be related to it, and so may the complex ores of the Tolwong mine on the Shoalhaven River.

In the Yass-Burrinjuck area are granites and porphyrites intrusive into Silurian and Middle Devonian rocks, and they are perhaps to be regarded as Tabberabberan and are probably responsible for the small silver-lead and copper deposits of the area. The intrusions seem to be continued south to the Tumut River, Yarrangobilly, Lobb's Hole and the country at the head of the Goodradigbee River, where small deposits of copper and silver-lead are associated with them. Farther north the wolfram of Frogmore is in granite of possibly the same age. The great bathylith running from Kiandra past Adaminaby and through Berridale, the Kosciusko plateau and Dalgety into Victoria is most likely Tabberabberan though perhaps younger. Gold, copper and a little wolfram are found with it.

In eastern and central-eastern Victoria many of the big intrusions may be Tabberabberan, but they are not easily separable from those of Carboniferous age. The diorites, intrusive into Lower Devonian beds, which brought in the gold of the Diamond Creek, Queenstown and Warrandyte fields, north-east of Melbourne, are probably of this age, and so is the remarkable swarm of dykes of intermediate to basic composition which follows the strike of the Silurian and Lower Devonian (?) beds of the Walhalla synclinorium in eastern Victoria; these are clearly related to the folding of the beds, which is Tabberabberan. The auriferous quartz-veins so abundant both in the dykes and in the folded sediments are comagmatic with the dyke-rocks. The gold-bearing granodiorites and porphyrites of the Strathbogie Ranges also seem to be Middle Devonian. As for the massive granites and associated gold deposits among the Ordovician schists of the north-east, it is very hard to tell their age; some of them are possibly Tabberabberan, and the same may be said for the copper and silver-lead at Buchan and Mt. Deddick.

In western Tasmania a series of granodiorites, porphyries and porphyrites, massive but passing into schistose phases, invades strata as high as Silurian and Lower Devonian, and may provisionally be regarded as Middle Devonian. With them came the deposits of copper, zinc, lead, silver and antimony in the Mt. Lyell, Zeehan, Rosebery and other fields.

Lower Carboniferous.

The Devonian passed into the Carboniferous Period with no orogenic interruption, but during and at the end of the Lower Carboniferous came the important Kanimblan epoch of folding, intrusion and metallogenesis. The whole of the Tasman geosyncline was affected save for a belt on the east coast of Queensland and New South Wales, and Kanimblan intrusions appear at intervals from the tip of Cape York Peninsula to the most southerly point of Tasmania. They show much magmatic differentiation and include very acid granitic types. With them are associated the gold deposits of Cape York Peninsula, and possibly those in the Hodgkinson and Herberton fields, at Croydon and Mt. Emu, and some of those of the Etheridge field. The extensive massive granites of the Charters Towers, Ravenswood and other neighbouring goldfields may belong to this epoch, though, as suggested above, they may be older. With the acid granites are associated the tin, wolfram and molybdenum ores of the Herberton region, and in the Herberton and Chillagoe fields there are silver-lead and copper. The Clermont and Mt. Wyatt goldfields may also be Kanimblan. There is some regional overlap between the Kanimblan and late

ORE REGIONS, PROVINCES AND DISTRICTS.

During any given metallogenetic epoch there was in general a variety of ores introduced. These, however acquired, may be looked upon as an integral part of the magma, intrusive or extrusive, with which they are associated. For the igneous rocks petrological kindreds and petrographical provinces have been determined by the prominence of certain elements or certain minerals of a common age in the component rocks, and in a similar way it may be found possible to distinguish ore provinces and ore regions. As it appears to be understood in this country, the term "ore province" has a purely geographical connotation, the question of age being ignored, perhaps because of a tacit assumption that the same magma with the same ore-constituents persisted under a given region throughout long intervals of geological time. But for the igneous rocks it has been shown that the petrological character of extrusions and intrusions has changed from time to time, and it does seem possible that a similar state of affairs may obtain for ore-deposits. Combining the considerations of space and time we may define an ore region as a major area within which

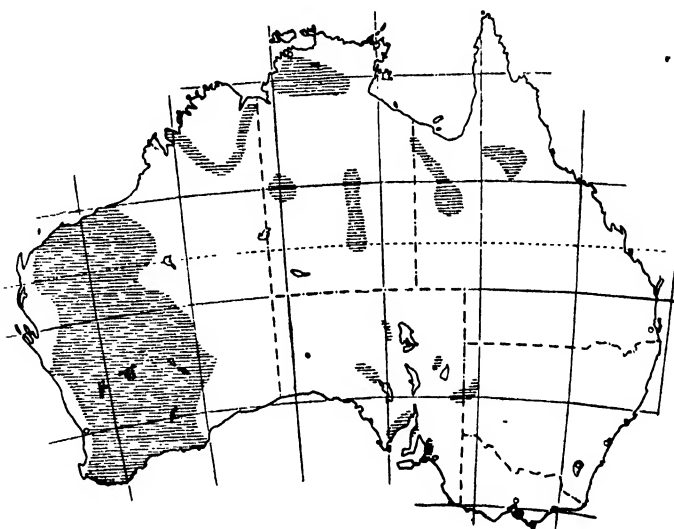


Fig. 2.—Pre-Cambrian ore regions and provinces.

ore-deposition occurred during a particular metallogenetic epoch. In general there will be a big variety of ores in such a region, but these are often segregated, and it may be possible to recognize smaller areas, either parts of an ore region or independent entities, characterized by dominance or predominance of ores of one or more elements; these we may call ore provinces, and even smaller and more specialized areas may be recognizable which may constitute ore districts. Since ore-deposition may have recurred several times in any given area, there may be overlapping of ore regions, provinces or districts of different geological epochs, and only a very intensive field-study will serve to differentiate them.

In Western Australia it is hardly possible to separate the pre-Cambrian ore regions of Pilbarian and Houghtonian age, but in the second of these epochs a large part of the State helped to constitute a very large ore region characterized by a general dominance of gold, with copper and iron almost as widely though by no means so abundantly distributed (Fig. 2). Simpson showed that in a coastal belt about 250 miles wide from West Kimberley to Norseman and Esperance there is a province abounding in lithium, beryllium, lanthanum,

cerium, tantalum and tungsten minerals. Some of these characterize separate ore districts; for instance tin and tantalum are associated in the south at Greenbushes, in the centre at Poona and Coodardy, and in the north at Moolyella, Wodgina and elsewhere in the Pilbara goldfield.

The pre-Cambrian ore-regions extend into North Australia, where gold and tin-tantalum provinces can be recognized, and the gold distribution extends far south into Central Australia.

In South Australia and western New South Wales there are provinces rich respectively in titanium and silver-lead and zinc, and the Moonta-Wallaroo area is a copper province. The Cloncurry ore-province of western Queensland is essentially a copper one with local concentrations of silver-lead and iron.

The Tyennan intrusions of Upper Cambrian time established an important copper province in the Mt. Lofty and Flinders Ranges, with gold and subsidiary ores of bismuth, molybdenum and uranium, which are in part restricted to separate districts. A copper-gold province was also constituted in the far

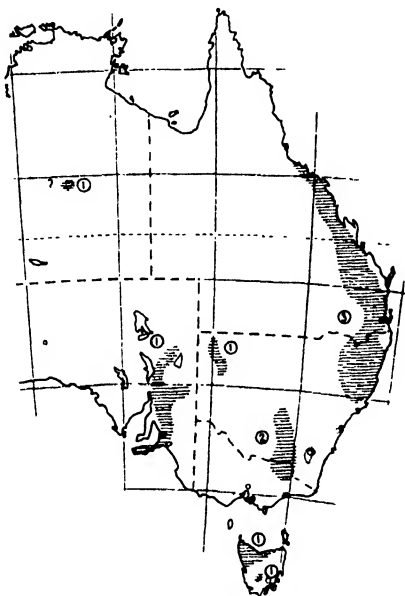


Fig. 3.—Upper Cambrian (1), Late Ordovician (2), and Late Permian (3) ore regions.

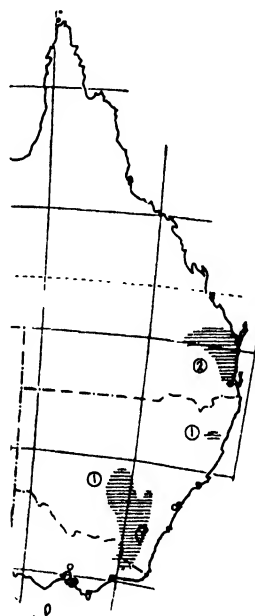


Fig. 4.—Late Silurian (1) and Late Cretaceous (2) ore regions.

north-west of New South Wales, and if the ultrabasic intrusions in the western half of Tasmania are of the same age, then this area also formed an Upper Cambrian ore-province with chromium, nickel and osmiridium (Fig. 3 (1)).

A late Ordovician (Benambran) gold-tin province seems to have been established in north-eastern Victoria and the adjoining parts of New South Wales, and may have extended in a north-north-westerly direction along the Western Slopes towards Condobolin (Fig. 3 (2)). The same general region may also have been a gold province in the late Silurian, and there were gold provinces and districts in the Central and Southern Highlands and on their western slopes as at Tuena, Adelong and Wyalong, also perhaps in New England. A long, narrow, iron-gold-copper province bordered the Murrumbidgee bathylith on the east and a linear province was constituted by the chromite and nickel of Gundagai, Berthong, Wallendbeen and other centres (Fig. 4 (1)).

To the Tabberabberan ore region of New South Wales and Victoria belong the gold-copper deposits of the Cobarr-Nymagee-Mt. Hope and the Forbes-Parkes provinces and the gold province of central-eastern Victoria from Queenstown and Warrandyte to Walhalla and Wood's Point. There was possibly a contemporary gold-copper province in western Tasmania and a gold province about Charters Towers (Queensland) (Fig. 5).

During the Kanimblan epoch eastern Australia contained a number of ore regions wherein several ore provinces and districts co-existed (Fig. 6). In the North Queensland region, for instance, which is broadly characterized by gold, there is the important Herberton-Chillagoe province with tin, silver-lead, copper, molybdenum and tungsten. To the same epoch may belong the Charters Towers (gold) and Clermont (copper-gold) provinces. The tin deposits of the country west of Cooktown mark a separate ore district. A linear iron province stretches along the coast between Mackay and the latitude of Maryborough.

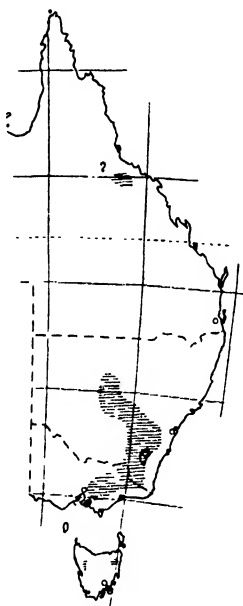


Fig. 5.—Late Middle Devonian ore regions and provinces.

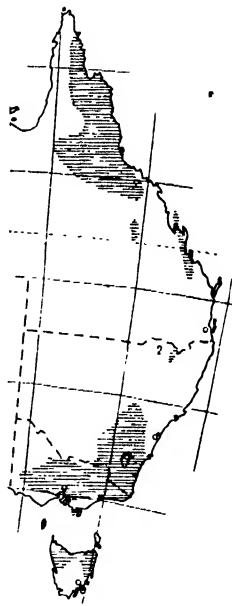


Fig. 6.—Ore regions of late Lower Carboniferous time.

The southern region contains copper and gold widely distributed in the Central and Southern Highlands and Western Slopes of New South Wales, and a tin province in which the Ardlethan deposits are prominent. Small gold districts are seen at Yalwal and Moruya, and the Bega batholith with its continuation into Victoria is marked by gold in the north and by molybdenum and bismuth farther south. The Victorian part of this region is essentially a great gold province in the western and central-eastern parts, with a few local concentrations of other metals, as of antimony at Heathcote and tin in the south-east.

At this time, too, an ore-province was formed in the northern half of Tasmania, wherein tinstone is the dominant economic mineral, with silver-lead, tungsten, bismuth and gold forming concentrations in various districts. This province is linked to Victoria through the King Island scheelite and the tin of Wilson's Promontory and, if the ultrabasic intrusions are Carboniferous and not Cambrian, by the osmiridium occurring at Waratah Bay.

[illegible]

resources of ores were dwindling, and stressed the need for an intensive search for new deposits. If a detailed study could be made of the extent and boundaries of the known ore regions, provinces and districts, and of the nature of their contained ores, with due regard to the epochs as well as the places of ore-introduction, much time and energy might be saved by directing the search to the most favourable places. Such a study would be no doubt lengthy and laborious, but at all events the policy would be systematic and scientific, and I venture to suggest that in the long run it would be justified by results.

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NITROGEN IN OIL SHALE AND SHALE OIL

XI. NITRILES IN CRACKED SHALE GASOLINE.

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In an unsuccessful attempt to detect thiazoles in the tar bases isolated from cracked shale gasoline by reductive cleavage with sodium and alcohol, followed by the detection of a mercaptan (Morton, 1946), it was observed that an appreciable amount of ammonia was liberated. Since this ammonia was free from both primary and secondary amines, it was possible that it had been derived from the hydrolysis of some constituent of the bases rather than by the reduction. Nitriles are present to a small extent in crude shale oil (Mapstone, 1949), and it would also be possible that small amounts may be formed during the thermal cracking of the crude oil for the production of the gasoline (Mapstone, 1948). Traces of hydrogen cyanide have been found in the cracked shale gasoline (Mapstone, 1946) and it may be considered as the simplest nitrile—formonitrile. The work described here was therefore carried out to determine, if possible the, amount of nitriles present in the bases.

DETERMINATION OF AMMONIA FROM THE HYDROLYSIS.

Barta and Marschek's observation that pyridine and its homologues could be separated from ammonia by distillation from a citrate buffer at pH 3.0 (Barta and Marschek, 1937, 1938) was used as a basis for the determination of the amount of ammonia liberated during the hydrolysis. Two hundred millilitres of redistilled tar bases isolated from the acid sludge from the treatment of the gasoline (Mapstone, 1947) were hydrolysed by 50 ml. of 10% sodium hydroxide solution in a distillation flask fitted with a reflux condenser and inclined so that no condensate could collect in the side arm. Since ammonia has a much lower boiling point than the tar bases, it could be distilled off continuously as formed. However, with the very small quantity of ammonia involved it was necessary to reduce to a minimum the amount of the pyridine homologues that distilled with the ammonia, as well as to provide a carrier to transfer the ammonia from the condenser to the absorption solution. This was achieved by periodically purging the contents of the condenser into 100 ml. of sodium phosphate-citric acid buffer of pH 3.0 (Hodgman, 1940) by passing a stream of ammonia-free air through the side arm of the flask. By reducing the heating rate so that the level of refluxing vapours was just above the side arm at the time of purging, the amount of pyridine homologues carried over with the ammonia was kept between 5% and 30% of the amount of ammonia evolved.

When the hydrolysis was considered to be complete after one to one and a half hours, 10% to 20% of the buffer solution were distilled into 100 ml. of 1% boric acid, and the pyridine homologues that had been absorbed along with the ammonia determined by titration of the distillate with 0.1 N acid. The ammonia was then determined by rendering the remainder of the buffer solution strongly alkaline with 40% sodium hydroxide solution and distilling into a fresh boric acid solution.

DETERMINATION OF ORGANIC ACIDS FROM THE HYDROLYSIS.

When cool, the dark brown layer of sodium hydroxide solution was separated from the tar bases, rendered strongly acidic with sulphuric acid, and distilled. The distillate was titrated with 0.1 N carbonate-free sodium hydroxide to a phenolphthalein end point for the determination of the organic acids. An appreciable amount of phenols was also present in the distillate.

The solutions containing the organic acids from all the analyses were bulked, acidified and distilled. The distillate was extracted with carbon tetrachloride to remove the phenols, neutralized with barium hydroxide, and evaporated to dryness. The dry barium salts were refluxed with ethyl alcohol and concentrated sulphuric acid; the sweet odour of the ester thus formed confirmed that the acids were organic. Three of five opinions were definite that the ester smelt like pineapple (ethyl valerate), and would therefore suggest that there was some valeronitrile (b.p. 141° C.) present in the bases.

DISCUSSION OF RESULTS.

Two samples of the bases were examined: one which had been isolated about four years previously, and another which was freshly isolated for this work. In each case the analysis was carried out in duplicate. The agreement between the amounts of ammonia and organic acids obtained (Table 1) indicates that they were liberated in equivalent quantities during the hydrolysis, and that their precursors were most probably nitriles.

The small amount of nitriles thus found to be present in the tar bases is equivalent to approximately 0.05% by volume (calculated as valeronitrile). Since the bases are present to an extent of only 0.3% by volume in the cracked shale gasoline, the nitriles found are equivalent to approximately 1.5 p.p.m. in the gasoline. In connection with some other work, it was found that a single wash with 10% of concentrated sulphuric acid completely extracted 0.5% of benzyl cyanide from crude shale oil, so it is probable that the whole of the nitriles in the cracked shale gasoline were concentrated in the sludge from which they would be isolated along with the tar bases. The actual nitrile content of the untreated gasoline would no doubt be somewhat higher than the 1.5 p.p.m. found here as portion will probably have been hydrolysed by the caustic washes given the gasoline prior to acid treatment, and during the recovery of the bases from the acid sludge.

TABLE 1.
Hydrolysis of Bases.
(Results as milliequivalents per litre of bases.)

| Bases. | Ammonia. | Organic Acids. |
|-----------------------|----------|----------------|
| Old | 6.0 | 7.1 |
| Old | 3.9 | 2.7 |
| Old average | 5.0 | 4.9 |
| Fresh | 5.1 | 7.9 |
| Fresh | 6.9 | 5.7 |
| Fresh average | 6.0 | 6.8 |

SUMMARY.

The amounts of ammonia and organic acids obtained by the hydrolysis of the tar bases isolated from the acid sludge from the treatment of the gasoline indicate the presence of about 1.5 p.p.m. of nitriles in the original gasoline.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge the assistance of B. B. Mellor and K. Davidson in carrying out this work, and the permission granted by the management of National Oil Pty. Ltd., for the publication of this paper.

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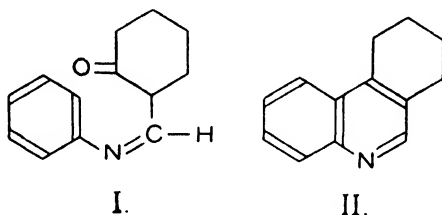
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THE CYCLIZATION OF ANILS OF β -KETO-ALDEHYDES.

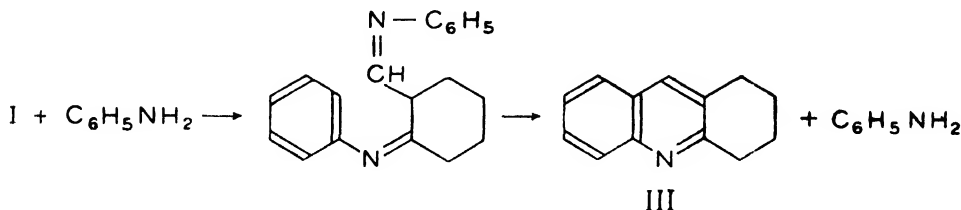
By G. E. CALF
and E. RITCHIE, M.Sc.

Manuscript received, May 23, 1949. Read, August 3, 1949.

It is well known that anils of β -diketones are readily cyclized by acidic reagents to 2:4-disubstituted quinolines (e.g. Combes, 1888; Roberts and Turner, 1927). It would therefore be expected that anils of β -keto-aldehydes would form 4-substituted quinolines, but so far attempts to effect such cyclizations have been unsuccessful (Claisen and Fischer, 1888; Thielpape, 1922) or have given very low yields (Romet, 1935). Borsche (1910) also failed to convert 1-(phenyliminomethyl)-cyclohexan-2-one (I) to the tetrahydrophenanthridine (II) by heating it with concentrated sulphuric acid at 100°, obtaining only the *p*-sulphonic acid of I and a similar result was obtained from the *m*-hydroxy derivative of I. However, since the successful cyclization of I would lead to an attractive phenanthridine synthesis, we have studied this reaction more fully.

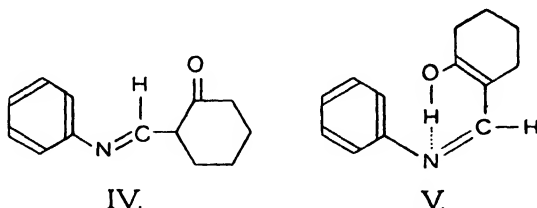


Numerous experiments were carried out in which I was treated with sulphuric acid of various concentrations at temperatures between 0° and 100°, but in each case it was either recovered unchanged or was sulphonated, and similar results were obtained with the methyl- and methoxy-derivatives of I. However, it was found that if these anils were refluxed with phosphorus oxychloride they were converted in 20–25% yield to bases which were identified as derivatives of 1:2:3:4-tetrahydroacridine (III). The same substances were formed, but in somewhat lower yields, by heating the anils with phosphorus pentoxide at 250° for a short time. The formation of these substances is best explained by the equations



which were originally suggested by Petrow (1942) to account for the formation of III when I was heated with aniline hydrochloride and zinc chloride in alcoholic solution.

The failure of anils of β -ketoaldehydes to cyclize normally has been explained by assuming that they exist in the *trans* configuration IV, which would be unfavourable to cyclization, rather than in the favourable *cis* configuration I. (Petrow, *loc. cit.*; Thielepape, *loc. cit.*)



However, no direct evidence for this assumption has been adduced and two strong objections may be made against it. Firstly, every analogy suggests that the anils are hydrogen bonded resonance hybrids, one of the chief contributing structures of which is shown by V, and which does have a configuration favourable to cyclization. Secondly, whatever the configuration of the anil itself may be, there is no reason to suppose that this configuration would be preserved in concentrated sulphuric acid (the usual cyclizing reagent). It appears then that some other explanation for the failure of anils of β -ketoaldehydes to cyclize smoothly must be sought.

EXPERIMENTAL.

The anils used in the following experiments were prepared by condensing *formyl*-cyclohexanone with aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-anisidine and *p*-anisidine respectively, in alcoholic solution (Petrow, *loc. cit.*).

Cyclization by Phosphorus Oxychloride.

The anil (10 g.) was gently refluxed with phosphorus oxychloride (30 c.c.) with exclusion of moisture for one hour. After cooling, the reaction mixture was poured into ice and water with vigorous stirring and when reaction ceased, filtered from resinous products. The filtrate was basified, extracted with ether and the product eventually isolated by distillation under reduced pressure in 20–25% yield. Final purification was effected by recrystallization from light petroleum.

Cyclization by Phosphorus Pentoxide.

An intimate mixture of the anil (10 g.) and phosphorus pentoxide (30 g.) was immersed in an oil bath maintained at 250° for fifteen minutes. After cooling, the reaction mixture was worked up as above, giving the tetrahydroacridine in about 10% yield.

The following tetrahydro-acridines, which were identified by their melting points, analyses (not quoted) and the melting points and analyses of their picrates (not quoted) were prepared by both of these methods: tetrahydroacridine m.pt. 56° (55°–56°), picrate m.pt. 220° (222°); 9-methyltetrahydroacridine, m.pt. 77° (77°–78°), picrate m.pt. 215°–216° (215°–216°); 8-methyltetrahydroacridine, m.pt. 100° (100°–101°), picrate m.pt. 186° (189°–190°); 7-methyltetrahydroacridine, m.pt. 62° (61°–62°), picrate m.pt. 189° (189·5°–190·5°); 9-methoxytetrahydroacridine, m.pt. 122° (121·5°–122·5°), picrate m.pt. 204° (206·5°–207·5°), and 7-methoxytetrahydroacridine, m.pt. 90° (90°–91°), picrate m.pt. 222° (223·5°–224·5°). The values given in brackets are those found by Petrow (*loc. cit.*).

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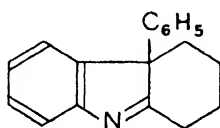
SOME REACTIONS OF AN ANGULAR PHENYL COMPOUND.

By K. H. B. GREEN and E. RITCHIE.

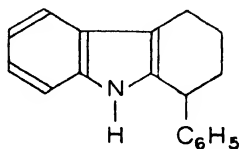
Manuscript received, May 23, 1949. Read, August 3, 1949

Substances containing an angular methyl group are well known from both natural and synthetic sources, but angular phenyl compounds are scarcely known. Allen and van Allan (1942, 1945) showed that when dimethyl-anhydroacetonebenzil was treated with acidic dehydrating agents it formed a bimolecular product containing an angular phenyl group. Allen, Bell, Clark and Jones (1944) prepared some naphthoquinone derivatives bearing angular phenyl groups and Boekelheide (1947) synthesized 9-phenyl decalin and 10-phenyl decahydroquinoline. However, very little is known of the reactions of such substances and since a characteristic reaction of the angular methyl group is its elimination on dehydrogenation, it was of interest to study the dehydrogenation and other reactions of an angular phenyl substance. The substance chosen was the readily accessible 11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine.

When the oily phenylhydrazone of 2-phenyl cyclohexanone was refluxed with glacial acetic acid a vigorous reaction occurred and 11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (I) was formed in good yield together with a smaller amount of 1-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazole (II). These substances are readily separated and distinguished from one another because I is basic and II is neutral. They were characterized by their yellow and reddish brown *picrates* respectively.

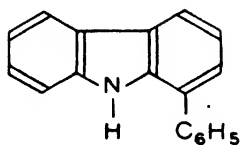


I.

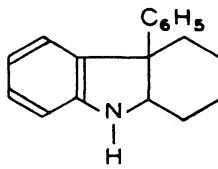


II.

Barclay and Campbell (1945) have shown that tetrahydrocarbazoles, and hexahydrocarbazoles especially, are smoothly dehydrogenated by chloranil to carbazoles. When their procedure was applied to II it readily yielded 1-phenyl-carbazole (III), but I which might be expected to split off benzene and hydrogen yielded only uncrystallizable tars under a variety of conditions. Similarly the dehydrogenation method of Perkin and Plant (1923), i.e. refluxing with sulphur in quinoline, gave only black resinous materials. Since hexahydrocarbazoles are much more readily dehydrogenated than tetrahydrocarbazoles, I was reduced by tin and hydrochloric acid to 11-phenyl-1 : 2 : 3 : 4 : 10 : 11-hexahydrocarbazole (IV) and its dehydrogenation by these methods attempted. But again only tars were formed.

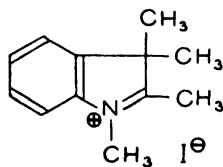


III.

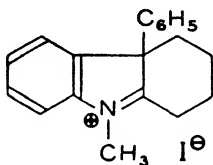


IV.

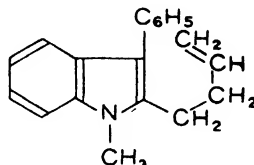
It has been shown (Ciamician, 1894) that when 2 : 3 : 3-trimethyl-indolenine-methiodide (V) is heated, it loses methyl iodide to form 1 : 2 : 3-trimethyl-indole. The similarly constituted 11-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine-methiodide (VI) however did not split off iodobenzene on heating, but instead gave a neutral substance, $C_{19}H_{19}N$, evidently formed by rupture of the reduced ring. It is probably 1-methyl-2-(Δ -3'-butenyl)-3-phenyl-indole (VII).



V.

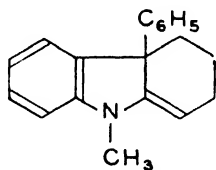


VI.

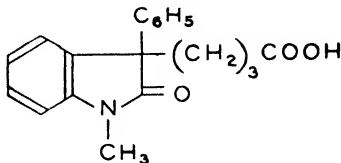


VII.

A few other experiments also were carried out on VI. When treated with sodium hydroxide it yielded a base which although rapidly turning purple on exposure to air could be distilled under reduced pressure. Treatment of the distilled base with hydriodic acid regenerated VI and by analogy with the behaviour of V with alkali (Brunner, 1900) it is formulated as 9-methyl-11 phenyl-2 : 3 : 4 : 11-tetrahydrocarbazole (VIII). Support for this structure was found in the observation that oxidation by permanganate produced an acid, $C_{19}H_{19}NO_3$, which must be 1-methyl-3-phenyl-3-(3'-carboxypropyl)-oxindole (IX)-



VIII.



IX.

EXPERIMENTAL.

11-Phenyl-1 : 2 : 3 : 4-Tetrahydrocarbazolenine (I) and 1-Phenyl-1 : 2 : 3 : 4-Tetrahydrocarbazole (II).

When phenylhydrazine (12.8 g.) and 2-phenyl cyclohexanone (20.8 g.) were warmed together on the water bath, water soon began to separate. After 20 minutes the mixture was cooled extracted with ether, the solution dried and the ether removed. The residual thick oil, which, could not be crystallized, was cyclized by refluxing it in glacial acetic acid (150 c.c.) for one hour. After diluting with water, the reaction mixture was basified and extracted with ether. The ether solution was then extracted with dilute hydrochloric acid, washed and dried.

The acid extract on basification yielded the carbazolenine (I) which after crystallization from aqueous alcohol formed colourless needles (14.5 g.) melting at 128°.

Found : C, 86.5 ; H, 7.0 ; N, 5.7%. Calculated for $C_{18}H_{17}N$: C, 87.5 ; H, 6.9 ; N, 5.7%.

The *picrate* crystallized from alcohol in yellow rhombs melting with decomposition at 185°.

Found : N, 11.9%. Calculated for $C_{24}H_{20}N_4O_7$: N, 11.8%.

The ether solution on evaporation gave a thick gum which could not be crystallized. However, it readily yielded a crystalline *picrate*, which on decomposition furnished the tetrahydrocarbazole (II) which then crystallized from aqueous alcohol in large colourless needles (1.4 g.) which melted at 98°.

Found : C, 87.0 ; H, 6.8 ; N, 5.7%. Calculated for $C_{18}H_{17}N$: C, 87.5 ; H, 6.9 ; N, 5.7%.

Its *picrate* crystallized from alcohol in dark brown needles melting at 131°.

Found : N, 11.8%. Calculated for $C_{24}H_{20}N_4O_7$: N, 11.8%.

1-Phenylcarbazole (III).

A solution of chloranil (2 g.) and the tetrahydrocarbazole (II ; 1 g.) in pure dry xylene (30 c.c.) was refluxed for 24 hours. After cooling, the tetrachloroquinol was filtered off and the filtrate washed with aqueous sodium hydroxide, dried and evaporated under reduced pressure. The residue crystallized from alcohol in colourless plates (0.65 g.) melting at 139°.

Found : C, 88.4 ; H, 5.5 ; N, 5.7%. Calculated for $C_{18}H_{13}N$: C, 88.9 ; H, 5.4 ; N, 5.8%.

Its *picrate* separated from alcohol in magnificent red needles melting at 153°.

Found : N, 12.1%. Calculated for $C_{24}H_{18}N_4O_7$: N, 11.9%.

11-Phenyl-1 : 2 : 3 : 4 : 10 : 11-Hexahydrocarbazole (IV).

The carbazolenine (I ; 5 g.), concentrated hydrochloric acid (10 c.c.), alcohol (10 c.c.) and tin (10 g.) were refluxed on the water bath for six hours. Whilst still hot, the supernatant liquid was decanted from undissolved tin into a large excess of dilute sodium hydroxide. The product, isolated by extraction with ether, was finally crystallized from aqueous alcohol separating as colourless needles (2 g.) melting at 118°.

Found : N, 5.6%. Calculated for $C_{18}H_{19}N$: N, 5.6%.

Its *picrate* crystallized from alcohol in yellow needles melting at 175°.

Found : N, 11.8%. Calculated for $C_{24}H_{22}N_4O_7$: N, 11.7%.

Methiodide of I.

When a solution of the base (I ; 5 g.) in methyl-iodide (15 g.) was allowed to stand at room temperature the product (VI) gradually separated. After three hours it was collected, washed with dry ether and recrystallized from aqueous alcohol separating as pale yellow prisms (6 g.) which on heating began to decompose at about 130°.

Found : N, 3.3%. Calculated for $C_{19}H_{20}IN$: N, 3.6%.

Pyrolysis of VI.

The methiodide (VI ; 5 g.) was gently heated with a free flame at 30 m.m. until decomposition began and the pressure rose rapidly. After the reaction had subsided, and the pressure had fallen, a light amber viscous oil was distilled over. Its solution in alcohol gradually deposited VII (1 g.) which was finally obtained as slightly yellow needles melting at 107°.

Found : C, 86.7 ; H, 7.2 ; N, 5.7%. Calculated for $C_{19}H_{19}N$: C, 87.4 ; H, 7.3 ; N, 5.4%.

Its *picrate* crystallized from alcohol in fine brown needles melting at 99°.

Found : N, 11.8%. Calculated for $C_{25}H_{22}N_4O_7$: N, 11.4%.

Action of Sodium Hydroxide on VI.

A solution of VI (5 g.) in hot water (200 c.c.) was treated with sodium hydroxide (10 c.c. of 10%) and the mixture cooled. The product (VIII) isolated by ether, distilled at 215°/3 mm. in almost quantitative yield as a viscous colourless oil. It crystallized on rubbing with light petroleum, but since it rapidly became purple on exposure to air further purification and analysis were not attempted. When treated with hydriodic acid VI was regenerated.

Its *picrate* crystallized from alcohol in yellow needles melting at 150°.

Found : N, 11.7%. Calculated for $C_{25}H_{22}N_4O_7$: N, 11.4%.

Oxidation of VIII.

A solution of potassium permanganate (1.5 g.) in water (15 c.c.) was gradually added to a boiling solution of VIII (5 g.) in acetone (15 c.c.). Reaction was rapid and after a short time the manganese dioxide was filtered off, washed with water and the combined filtrates evaporated to a small bulk. Acidification then precipitated IX which crystallized from aqueous alcohol in colourless needles (2.1 g.) melting at 146°.

Found: N, 4.5%. Calculated for $C_{19}H_{19}NO_3$: N, 4.5%.

ACKNOWLEDGEMENT.

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ANODIC AND CATHODIC POLARIZATION OF COPPER IN ACETIC ACID.

By R. C. L. BOSWORTH, Ph.D., D.Sc.

With five figures.

Manuscript received, July 13, 1949. Read, September 7, 1949.

INTRODUCTION.

In a series of papers the author (Bosworth, 1949) has described an attempt to apply the principles of dimensional analysis to metallic corrosion. From studies of the rates of corrosion under standardized conditions of forced and natural convection it was found that five properties were concerned in determining the rate of corrosion for a given system under given external conditions. These properties were :

- (a) A maximum corrosion rate (q_0) given by the rate at which corrosion would proceed were all limitations due to slow diffusion or convection made negligibly small.
- (b) A conductivity term (j) equal to the rate at which the liquid acting as the corrodant would allow the controlling depolarizing agent to flow to the surface under unit driving force or potential difference for the type of flow concerned.
- (c) A capacity term (K), or the change in the driving force for unit change in the concentration of the depolarizing agent produced by means of the corrosion reaction.
- (d) The density change produced by unit change in the concentration of the depolarizing agent, and
- (e) The driving force (E) for the corrosion reaction.

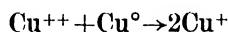
However, the experiments already described were capable of giving only four independent properties. They gave no measure of E and further gave only j and K figures in terms of the products jE and KE respectively. It thus appears desirable that some method of estimating E for the systems considered earlier be investigated.

The quantity E , if it is to be a measure of the potential for the flow of the depolarizing agent from bulk of the corrodant liquid to the metal surface, must clearly be some measure of the work done in taking unit quantity of the agent from a combined state on the metal surface, and, completely undoing all associated chemical reactions at constant temperature and pressure, take it to a free state in the bulk of the corrodant liquid. If the flow is to be measured in terms of the movement of any essential reagent concerned in the corrosion reaction the associated potential could be measured in terms of the work done (multiplied if necessary by any convenient, but constant, factor) in allowing unit quantity of the reagent concerned to be taken from metal surface to bulk liquid by a reaction which undoes the process of corrosion. Since the flow has been recorded in terms of the passage of unit mass of metal from surface to liquid, the potential is obviously a measure of the work done to send unit mass of metal back again to the surface, and this is equal to the (non-molar) Gibbs' free energy

for the particular reaction concerned. A measurement of the e.m.f. which just balances the tendency of the metal to dissolve is, at constant temperature, a constant multiple of this quantity.

The effective e.m.f. given by an electrode placed in an electrolyte with which no approximately reversible chemical change is possible is (as pointed out by Gatty and Spooner, 1938, p. 23) the net effect of two possible exchanges between the metal and the electrolyte. In one the metal is behaving anodically and supplying positive ions to the solution, and in the other it is behaving cathodically and receiving positive ions from the solution. If the two reactions when balanced electrically, as they must be when the charge on the electrode has ceased to change, are not balanced chemically, then a net reaction must take place at the surface. This net chemical reaction can always be balanced against a net electrical potential obtained by making the anodic areas more negative and thus repressing the dissolution of metallic ions, and by making the cathodic areas more positive and thus repressing the deposition of hydrogen ions. Direct measurement of the external potential difference between the anodic and cathodic areas required to repress the reaction is not possible and an indirect method must be devised. The method adopted was that of measuring, as a function of the current, the p.d. between electrodes anodically and cathodically polarized and an unpolarized electrode to which no net current flowed and which therefore came to a potential with respect to the solution determined by electrical balance of the anodic and cathodic reactions. The polarizing current used is a measure of the rate of transfer of ions from the anodic to the cathodic areas, and the polarization is a measure of the internal resistance offered to this transfer. When the rate of transfer of ions is made electrochemically equivalent to the quantity q_0 then the arithmetic sum of the overpotentials must be equal to the required driving force E . In this paper we will be concerned only with a measure of the driving force for copper in acetic acid-acetic anhydride mixtures. Other systems could be studied in a similar manner.

To convert our q_0 values into the equivalent current density terms we require a knowledge of the valence of the copper ion actively concerned in the electrode reaction. Since experiments have shown that the rate of corrosion of copper in acetic acid is increased threefold or more by the addition of small amounts of cupric ions to the solution (for example by dissolving 1% of cupric acetate in the acetic acid), it is therefore reasonable to assume that the oxidation-reduction reaction



plays at least an important part in the anodic attack. On this basis we may write the current density (i) in amperes per sq. cm. as electrochemically equivalent to a corrosion rate of

$$5.69 \times 10^6 \ i \text{ mgms. dm.}^{-2} \text{ day}^{-1}$$

So that if we find the sum of the two overpotentials when i is made equivalent to the recorded values of q_0 we have a means of deducing the driving force, or corrosion cell e.m.f.'s E .

Quite apart from this use of the experimental data to give a quantity concerned in corrosion problems in acetic acid media, the general behaviour of polarized electrodes in non-aqueous solvents is a subject which is now receiving some attention, particularly at the hands of Bockris (1947) and his collaborators.

EXPERIMENTAL.

Since the complete curves of anodic and cathodic overpotential versus current density were required, and further since the electrolytes to be used were often of very low electrical conductivity, the commutator method was employed.

An outline of the circuit diagram is given in Figure 1. In this circuit a battery B drives a primary current through a milliammeter A, controlling resistance R, standard set of resistances (decade box) S, and triple gang commutator C_1 , C_2 , C_3 to the triple electrode system E_1 , E_2 , E_3 . E_1 was the cathode, E_3 the anode, and E_2 a reference electrode. The milliammeter A was used only in setting a suitable value for the polarizing current. The value of the current was determined by measurement of the p.d. across S. During that commutator half cycle for which no primary current flowed in the electrode circuit the electrodes were connected to the triple throw, double pole switch T, the reference electrode and cathode to T_1 and the anode and reference electrode to T_2 . The third pole T_3 of the switch was connected across the standard resistance S only during the half cycle for which primary current is flowing, for the other half of the cycle T_3 was an open circuit. The switch terminals lead to a potentiometer which thus could measure the polarizing current (p.d. across S), the cathodic polarization (p.d. between E_2 and E_1) or the anodic polarization (p.d. between E_3 and E_2).

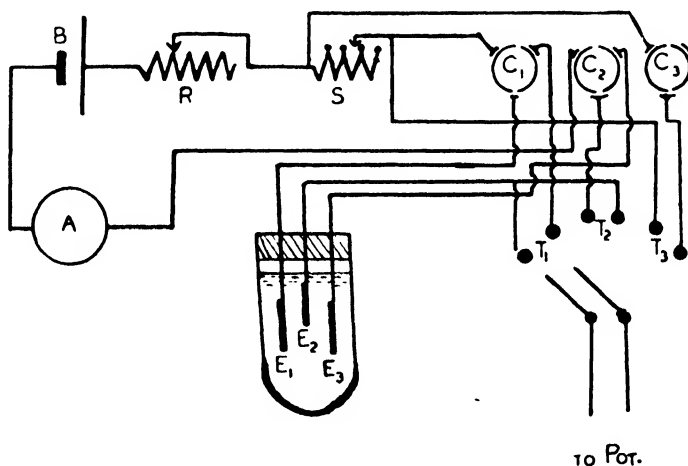


Fig. 1.

The electrodes were of copper strip 1.25 cm. wide and immersed 4 cm. in the electrolyte. The copper surfaces were prepared by polishing with gauge 0 emery paper followed by heating to dull redness and quenching in alcohol. The electrolytes used were 50% and 80% aqueous acetic, glacial acetic acid (95%) and acetic anhydride. In the former two electrolytes the battery B was a six-volt storage battery and in the latter two a two hundred-volt battery eliminator was used with suitable modification to the resistances.

The mechanical commutator method as here used has been regarded with suspicion when used with the more usual aqueous solutions on account of the decay of the polarization current during the "off" cycle of the commutator. Here where we are dealing with solutions of high electrolytic resistivity, low ionic concentration and high permittivity, it is to be expected that the time of discharge of the surface double layer will be large. Indeed the use of various commutator speeds from 40 to 400 r.p.m. have shown that the polarization curves in the liquid of lowest resistivity (the 50% acetic acid) are independent of the commutator speed over this range.

The Polarization Curves.

The experimental results for the current density versus anode and cathode polarizations are shown in Figure 2. The current density recorded is that for the charging half cycle only, and not the average value over the whole cycle as read by the milliammeter A. Several interesting features emerge from these graphs. In the non-aqueous solutions the anodic and cathodic polarizations are approximately equal at equal current densities (i). The measured polarizations are not exactly the same as normal overvoltages which are measured against a reversible reference electrode, whereas the reference electrode in the present experiments is at a non-reversible corrosion potential. Nevertheless the measured polarization (V) will differ only slightly in magnitude for normal anodic and cathodic overvoltages, and certainly the sum of the two polarizations will be equal to the sum of the anodic and cathodic overvoltages.

In all four cases of polarization in the non-aqueous solvents a plot of $\log i$ versus $\log V$ gave satisfactory straight lines. These lines are shown in Figure 3. From the slopes of these lines we may calculate factors α defined as

$$\alpha = 2.303 \frac{RT}{F} \frac{d \log i}{d \log V} \dots\dots\dots (1)$$

The factors α and the quantities i_0 (the antilogs of the intercepts) calculated from the curves shown in Fig. 3 are given in Table 1.

TABLE I.
Polarization of Copper at 27° C.

| Electrolyte Used. | Anodic Polarization. | | Cathodic Polarization. | |
|------------------------|------------------------------------|----------|-------------------------------------|----------|
| | i_0 in amps. cms. ² . | α | i_0 in amps. cms.- ² . | α |
| Glacial acetic acid .. | 7.1×10^{-7} | 0.184 | 7.6×10^{-7} | 0.168 |
| Acetic anhydride .. | 4.5×10^{-7} | 0.127 | 4.5×10^{-7} | 0.102 |

Collected data on the two factors i_0 and α have been given by Bowden and Agar (1938). For cathodically polarized copper in aqueous mineral acids i_0 ranges from 10^{-5} to 10^{-6} and α from 0.8 to 0.5. Similar values of α have been recorded for oxygen overvoltages (Bowden, 1929), while smaller values of the order 0.25 were recorded by Bowden and Kenyon (1935) for hydrogen overvoltages in alkali solutions. Since α measures the rate of variation of the activation energy for deposition of ions with the external field, it has been concluded that the mechanism for deposition of hydrogen (cathodic overvoltage) is different in alkaline solution from that in (aqueous) acids. The figures recorded above for the non-aqueous conductors examined indicate still lower values for α and thus still less dependence of the activation energy for the deposition of ions on the external field.

In the more nearly aqueous solutions the curves of Fig. 2 show an anodic polarization much less than the cathodic. In the 50% solution the cathodic polarization remains quite small until a current density of the order 10^{-5} amp. cms.-² is reached when the polarization increases rapidly with further increase in the current density obtaining a maximum value of 0.74 volt and thereafter *decreasing* with further increase in the current density in such a way that the sum of the two polarizations remains constant and equal to 0.79 volt. The

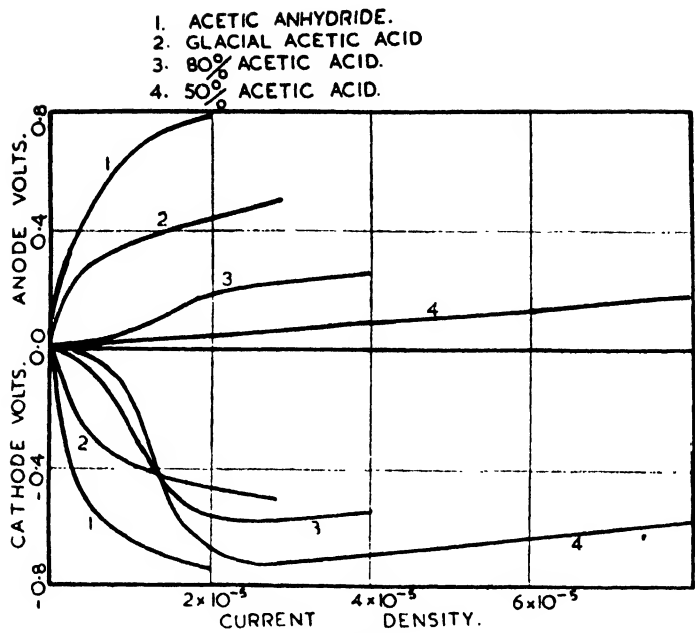


Fig. 2.

behaviour of the 80% solution is in a way intermediate between that of the 50% and the 95% solution, showing a less abrupt rise in the cathodic polarization and intermediate values for the anodic polarization. Detailed examination of the polarization curves show that neither of these solutions follow the exponential law

$$V = b(\log i - \log i_0)$$

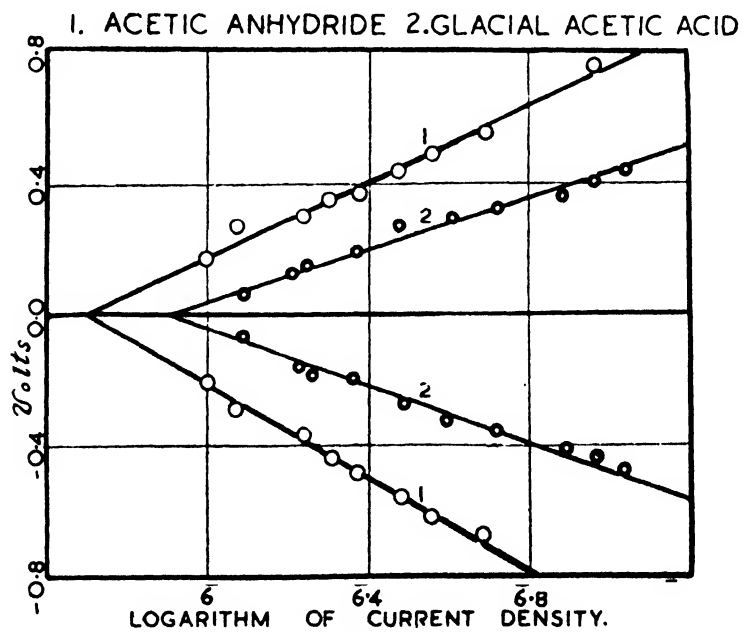


Fig. 3.

even approximately over any appreciable range. It is accordingly impossible to derive values of α or i_0 for these systems.

The data as given in Figure 2 refer to unstirred solutions initially saturated with air. Solutions prepared by boiling and cooling in a stream of hydrogen gave substantially the same curves. The act of stirring the electrolyte had but little effect on the anodic overpotential, but produced a very severe reduction of the cathodic overpotential in the region of current density in which the overpotential is rapidly rising. After a change in current density the overpotential generally settled down within a minute or two to the final new value. Again, however, in the case of the cathode in the region of rapidly changing overpotential the value at any fixed current density increased with time over a longer period and approached the final value only after about 20 minutes. The depression produced by stirring was again only of a temporary nature and the original value was restored on standing.

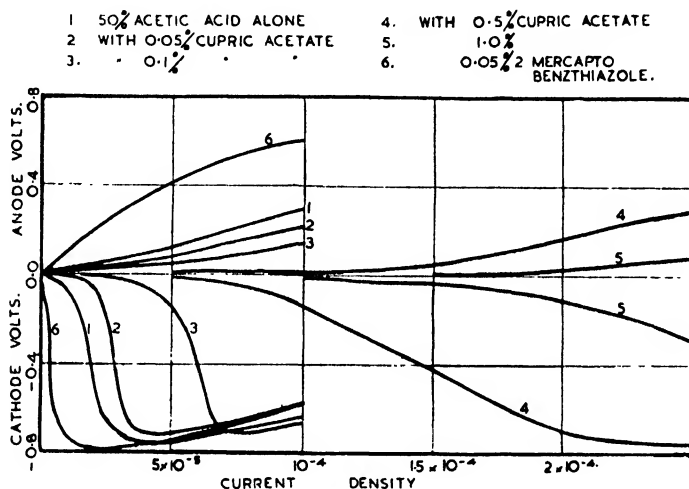


Fig. 4.

There was, however, a limit to which the effect of slow changes could be studied in these systems. On standing the copper electrodes slowly dissolved in the acetic acid, and since the presence of copper acetate in solution profoundly modified the nature of the polarization curves it was necessary to change the acid at fairly frequent intervals, particularly when dealing with high current densities. The effect of cupric ions on the polarization curves in 50% acetic acid is shown in Figure 4, where the polarization curves are given for systems with various quantities of cupric acetate added. At any fixed current density the addition of cupric acetate lowers both anodic and cathodic overpotential and also moves the point of rising cathodic overpotential into progressively higher and higher current densities. Cupric acetate is a corrosion accelerator in this system.

The opposite effect is shown by mercapto-benzthiazole, a corrosion inhibitor for copper. The addition of 0.05% of this substance both raises the overpotential and shifts the region of rapidly changing cathodic overpotential to lower current densities. A polarization curve for copper in 50% aqueous acetic acid with the addition of 0.05% of 2-mercaptobenzthiazole is also shown in Figure 4.

So far no chemical interpretation of the anodic and cathodic reactions concerned in the polarization observed in these liquids has been attempted. All the anodic polarization curves and the cathodic curves for glacial acetic acid and for acetic anhydride follow, as has already been indicated, a Tafel equation. However, the form of the cathodic polarization curves for the 50% and 80% aqueous acetic acid resembles that of a polarographic curve and strongly suggests that a change in the mechanism of the transport of the electrical charge occurs over a comparatively narrow range of current densities, the change involving the replacement of ions of comparatively low overvoltage by those of higher overvoltage as effective carriers to the cathode surface. Such a change, for example, might consist in the replacement of copper ions, originating from copper dissolved at the anode, by hydrogen ions when the current density becomes too heavy for transport by the attenuated array of copper ions. If this interpretation is correct a linear relationship is to be expected between the concentration of copper ions and the current density at which the change in the nature of the cathodic reaction occurs. Figure 5 shows the concentration of

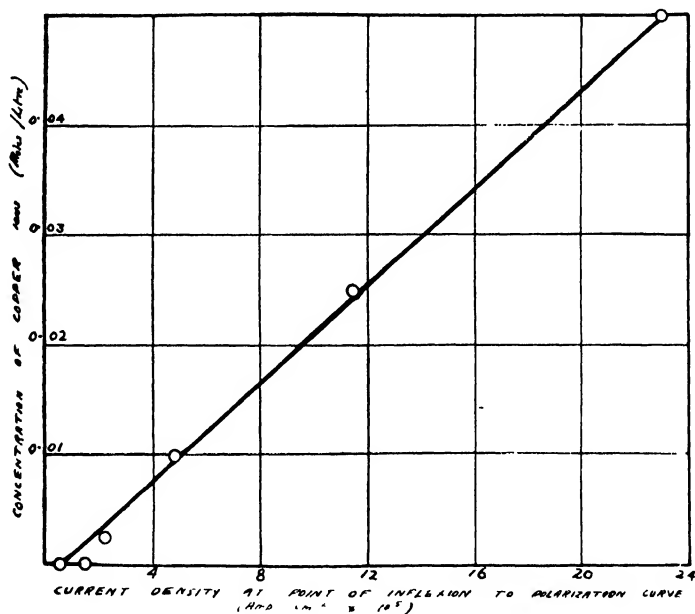


Fig. 5.

cupric ions $C_{Cu^{++}}$ plotted against the current density i_{crit} required to give the point of inflexion on the cathodic polarization curve. The data used were those obtained from Figure 4. Figure 5 shows a linear relationship between $C_{Cu^{++}}$ and i_{crit} . The extreme left-hand point on the figure refers to the solution of 2-mercaptobenzthiazole and an interpretation of the effect of this substance on the cathodic polarization curves now becomes clear. 2-Mercaptobenzthiazole forms a stable complex with cupric ions and thus reduces the current density which may be carried by these ions.

From the slope of the line shown in Figure 5 it will be seen that

$$\frac{d i_{crit}}{d C_{Cu^{++}}} = 4.5 \text{ amps. cms. moles}^{-1}.$$

Now it may readily be shown by solution of the Fick diffusion equation (see for example Kolthoff and Lingane, 1941, p. 435) that the limiting diffusion current is given by

$$\frac{d i_{\text{crit}}}{d C} = \frac{D}{\delta} z F,$$

where D is the diffusion coefficient for the ions deposited,

δ is the thickness of the diffusion layer at the electrode,

z is the valence of the ions ($z=2$ for cupric ions), and

F is the Faraday.

The diffusion coefficient for copper ions in dilute aqueous solution is given (Kolthoff and Lingane, p. 45) as 7.2×10^{-6} cms.² secs.⁻¹. It is not expected that the value would be very different in dilute solution in acetic acid. Frenkel (1946) has remarked on the striking constancy of the diffusion coefficients in different liquid solvents. Accordingly we may use the equation above to derive an approximate value for the effective diffusion layer thickness (δ), namely

$$\delta = 0.3 \text{ cm.}$$

which may be compared with the figure of 0.03 cm. quoted by Glasstone (1941) as a typical diffusion layer thickness for unstirred solutions at room temperatures. The deduction thus appears to lend considerable support to the suggestion that the lower part of the cathodic polarization curves is associated with the discharge of cupric ions.

The upper part of the polarization curves in these same solutions is presumably due to hydrogen deposition. Here also no equation of the Tafel form appears to be applicable. Indeed the measured overvoltage in all cases drops with further increase in the current density, suggesting, on taking the observations at their face value, that the hydrogen film formed at the higher current densities is electro-negative in character, similar, for example, to the hydrogen films formed on tungsten *in vacuo* (Bosworth, 1937).

However this apparent drop in the cathodic overvoltage may or may not be real. The commutator method of investigation used in this work is known to give low figures at high current densities (Ferguson, 1947). Use of the direct method of measurement in this work was excluded on account of the high resistivity of the liquids under test. In some cases the total p.d. between anode and cathode (net polarization plus ohmic drop in solution) was over 200 volts during the charging half of the commutator cycle, while the total measured polarization during the open half of the commutator cycle was less than one volt. The time constant for the decay of the overvoltage film is equal to the product of the resistance and the capacity, both measured per unit area of electrode surface. Bowden and Grew (1947) have found an electrostatic capacity (for a mercury-sulphuric acid interface) of $20 \mu\text{F cm.}^{-2}$ and other workers have reported figures of a similar order of magnitude. As mentioned above, the resistivities of the liquids used in this work were abnormally high, ranging from 40,000 to 10,000,000 ohms per square centimetre of the electrode surface. It is thus to be expected that the time constants for the decay of the overvoltage films would be of the order 0.8 to 200 seconds. Since the commutator remained in the "open" condition for only 0.2 secs., it is not to be expected that errors due to rapid decay would be appreciable except, possibly, in the more highly conducting liquids (50% aqueous acetic acid with copper acetate in solution) and at the highest current densities, and it is only here that difficulties in the interpretation of the results were experienced.

The Corrosion Cell E.M.F.'s.

The corrosion cell e.m.f.'s for copper in these liquids may be derived from the curves shown in Figure 2. Data were first obtained for the rate of corrosion of copper specimens, from the same batch as the electrodes, at 27° C. and in acetic anhydride, acetic acid and 50% aqueous acetic acid. The test surfaces consisted of plane faces surrounded by a "guard ring" of the same metal, held horizontal and immersed at different depths (z) below the free surface of the corrodant. The rate of dissolution q of the face (in milligrammes per square decimetre per day) was measured as a function of z and by extrapolation to zero z a corrosion rate q_0 is found which is assumed to be the rate when there is no limitation of the chemical attack due to slowness of the diffusion to or from the surface. Details of these measurements have already been given (Bosworth, 1949). The values of q_0 are then converted into equivalent current densities. The sum of the overvoltages at these current densities was then read off from Figure 2 and this sum was taken as a measure of the corrosion cell e.m.f. The results thus obtained are given in Table II. It will be noted in particular

TABLE II.
Maximum Corrosion Rates and Cell E.M.F.'s for Copper.

| Electrolyte. | q_0 . | Equivalent Current Density. | Cell E.M.F. |
|---------------------------|---------|---|-------------|
| Acetic anhydride | 51 | 9.0×10^{-6} amps. cms. ⁻² | 1.30 volts |
| Glacial acetic acid | 100 | 17.7×10^{-6} | 1.00 .. |
| 50% acetic acid | 97 | 17.1×10^{-6} | 0.70 .. |

that the value for q_0 in 50% acetic acid is beyond the inflexion of the cathodic polarization curve. This must clearly be so as the deposition of cupric ions cannot be the cathodic reaction in the corrosion of copper.

SUMMARY.

The cathodic and anodic overpotentials of copper in 50% and 80% aqueous acetic acid, in glacial acetic acid and in acetic anhydride have been measured as a function of the current density by the commutator method, it having been shown that the time constants in these poorly conducting media are long.

The two non-aqueous liquids gave polarization curves of the logarithmic type. The dimensionless factors $\alpha \left(2.303 \frac{RT}{F} \cdot \frac{d \log i}{dV} \right)$ calculated from the slopes

are only of the order 0.10 to 0.18, the anodic value being slightly lower than the cathodic. These low figures indicate that the activation energy for the deposition of ions in these solvents are much less effected by external fields than in aqueous solutions.

In 50% aqueous acetic acid the cathodic overpotential shows a sudden rise over a narrow range of current densities. The current density at which this rise occurs is directly proportional to the concentration of cupric ions present in the acetic acid solution. The addition of 2-mercaptobenzthiazole which lowers the concentration of free cupric ions produces a high cathodic polarization at very low current densities and incidentally is a very effective corrosion inhibitor.

Corrosion cell e.m.f.'s have been deduced from a combination of the over-voltage curves with independently measured corrosion rates. These e.m.f.'s

are : 1.3 volts, copper in acetic anhydride ; 1.0 volts, copper in glacial acetic acid ; and 0.7 volt, copper in 50% aqueous acetic acid.

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THE CHEMISTRY OF RUTHENIUM.

PART III. THE REDOX POTENTIALS OF THE RUTHENIUM II COMPLEXES WITH SUBSTITUTED DERIVATIVES OF 2 : 2' DIPYRIDYL AND O-PHENANTHROLINE.

By F. P. DWYER, D.Sc.

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In a previous paper (Dwyer, Humpoletz and Nyholm, 1946) the preparation of the tris o-phenanthroline ruthenium II salts was described, and the potential of the reaction $\text{Ru(phenan)}_3^{+++} - e' \rightarrow \text{Ru(phenan)}_3^{+++}$ was determined. The potential was found to decrease with increasing acid concentration, and was notably unstable except in concentrated acid solution. The instability was undoubtedly due to auto-reduction of the oxidant ion, since the blue solution of the oxidised material became orange red—the colour of the original ruthenium II compound—on standing for a short time. It thus appeared that phenanthroline itself, whether freed by dissociation or bound to the ruthenium, was capable of being oxidised at the high potentials operating in the weakly acid solutions. The potential of the system in 0.1 normal acid, 1.29 volts, was lower than that found for the corresponding 2 : 2' dipyridyl compound (Steigman, Birnbaum and Edmonds, 1942), although by analogy with the ferrous compounds (Dwyer and McKenzie, 1947) the phenanthroline complex was expected to have the higher value.

With small samples of various substituted derivatives of 2 : 2' dipyridyl and o-phenanthroline, made available by Dr. A. Albert, a further study has been made of the ruthenium compounds, and at the same time the potentials of the 2 : 2' dipyridyl and o-phenanthroline complexes themselves have been determined by a more reliable procedure. Although the evaluation of redox potentials by the titrimetric method does not give highly accurate results (Dwyer, Nyholm and McKenzie, 1944), the instability of the oxidised form of most of the ruthenium complexes precludes the standard procedure of allowing an electrode to come to equilibrium in an equimolar mixture of the pure oxidant and reductant, and hence some titrimetric procedure must be used. The most reliable of such methods due to Smith and Richter (1944) involves the use of an accurately standardised solution of the reductant, to which is added sufficient of the oxidising agent to convert exactly one-half to the oxidised form. The oxidising agent is selected so that its potential is at least 0.2 to 0.3 volt higher than the redox potential of the substance under examination. The potential of a suitable electrode in such a mixture is found to rise rapidly to a maximum, which persists for a variable time depending on the stability of the oxidised form. The maximum potential represents the most probable value of the true redox potential. In the present study this method has been used for the ruthenium II complexes with 2 : 2' dipyridyl and o-phenanthroline, but with the substituted derivatives which were available in only small amounts the usual titrimetric method was used.

It has been found that, over a wide range of acidities, the complex with o-phenanthroline had always a slightly higher potential than the 2 : 2' dipyridyl complex. The substituted derivatives followed the same trend with ruthenium

as with ferrous iron (Smith and Richter, *loc. cit.*). Thus the presence of methyl substituents, which raise the basicity of the chelate group, lowered the potential; whilst bromo substituents which have the opposite effect on the basicity, raised the potential. The presence of methyl substituents in both the parent bases lowered the stability of the oxidised form of the complex, probably by oxidation of such groups. The complex derived from 5-bromo o-phenanthroline, which had the extremely high redox potential of 1.41 volts, was the most unstable of all in the oxidised form. In this compound it is possible that the phenanthroline ring is attacked at the high potential.

EXPERIMENTAL.

Ruthenium II Complexes. These were prepared in a similar manner to the tris-o-phenanthroline compound, described previously (*loc. cit.*) by refluxing an aqueous solution of potassium pentachloro-hydroxy ruthenate IV (1 mol.), with the base (3 mols.), until a greenish brown solution resulted, and then adding a few drops of 30% hypophosphorous acid just neutralised with caustic soda. The heating was continued until the colour had changed to deep orange red, when the mixture was filtered, and potassium iodide added. The compounds then crystallised in orange to orange-red needles or prisms. They were recrystallised from hot water, and dried over concentrated sulphuric acid. The bases used were 2:2'-dipyridyl, 4:4'-dimethyl-dipyridyl, 5:5'-dimethyl-dipyridyl, 5-methyl-o-phenanthroline, 5-bromo-o-phenanthroline and 5-nitro-o-phenanthroline. Tris-5-bromo-o-phenanthroline ruthenium II iodide could not be obtained pure, presumably owing to reduction of the nitro group by the sodium hypophosphite. Under the conditions of drying employed, the compounds derived from 2:2'-dipyridyl and its substituted derivatives were the pentahydrates, whilst those derived from o-phenanthroline were tetrahydrates.

TABLE I.
Ruthenium Compounds: $RuB_3I_2 \cdot 4$ or $5H_2O$.

| Base. | M.P. | Calculated. | | | Found. | | |
|---|------|-------------|------|------|--------|-----|-----|
| | | C. | H. | N. | C. | H. | N. |
| 2:2' dipyridyl | 71° | 39.4 | 3.45 | 8.98 | 39.3 | 3.4 | 9.1 |
| 4:4' (CH ₃) ₂ dipy. .. | 169° | 43.28 | 4.59 | 8.42 | 43.4 | 4.3 | 8.5 |
| 5:5' (CH ₃) ₂ dipy. .. | 114° | 43.28 | 4.59 | 8.42 | 43.2 | 4.7 | 8.6 |
| 5-CH ₃ -o-phen. | 112° | 46.35 | 3.75 | 8.32 | 46.4 | 3.5 | 8.3 |
| 5-bromo-o-phen... .. | 117° | 35.85 | 2.40 | 6.97 | 35.7 | 2.3 | 7.2 |

The iodides were transformed to the more soluble nitrates by dissolving in a small amount of hot water and adding a slight excess of silver nitrate. The mixture was evaporated to dryness to coagulate the silver iodide and to prevent the formation of complexes of the type $Ru(phenan)_3(AgI_2)_2$. The mass was then extracted with water, the silver iodide filtered out, and the solution made up to M/200. The nitrates and sulphates of the complexes with 5-bromo and 5-methyl-o-phenanthroline were so sparingly soluble that the solution were made M/400.

Apparatus and Procedure. The redox apparatus consisted of a small beaker, fitted with a stopper, carrying a platinum foil electrode, an ammonium nitrate salt bridge, tubes for the ingress and outlet of carbon dioxide, and a micro burette. The potential of the saturated calomel electrode at 15° C. was taken as 0.2500 volt.

The complex ruthenium compound (5 c.c.) was mixed with distilled water, and nitric acid and the total volume made up to 14 c.c. Since the amount of oxidising agent required for half oxidation was 1.0 to 1.2 c.c., the concentration of ruthenium solution at the equimolar point was M/600, except with the 5-bromo and 5-methyl-o-phenanthroline compounds, when it was M/1200. The mixture was stirred with a rapid stream of purified carbon dioxide, and cooled to 0° C. in an ice bath. The oxidising solution of ceric nitrate was 0.02 N approximately, in nitric acid of the same concentration as the ruthenium complex. It was standardised each time immediately before addition to the ruthenium solution, using a fresh solution of ferrous ammonium sulphate as the standard.

The determination of the redox potentials of the 2:2' dipyridyl and o-phenanthroline compounds was made by adding the calculated volume of the oxidising agent for half oxidation as rapidly as possible, and immediately reading the potential on the platinum electrode. The potentials rose rapidly during the first one to two minutes and then remained stationary for a varying time before falling. The highest potential was taken as the redox potential. The potentials of the substituted compounds were obtained by rapid titration until (approximately) the substance was half oxidised, when it was done more slowly, accepting the highest value, and then rapidly to the end point. From the end point titration, the point of half oxidation was calculated in the usual way. Except with the 2:2' dipyridyl compound, which was the most stable, the potentials are not considered more accurate than ± 5 mv. The results are shown in Table II.

TABLE II.

The Redox Potentials of the Ruthenium II Complexes with Substituted Derivatives of 2:2' Dipyridyl and o-Phenanthroline in Nitric Acid.

| Acid Concen- tration Normality. | E _h . | | | | | |
|--|-------------------------|-------------------|---|---|---|---------------------------|
| | 2:2' dipy. Volts. | Phenan. Volts. | 4:4' (CH ₃) ₂ Dipy. Volts. | 5:5' (CH ₃) ₂ Dipy. Volts. | 5-(CH ₃) Phenan. Volts. | 5-Br Phenan. Volts. |
| 0.002 | 1.303 | 1.31 | 1.152 | 1.240 | 1.29 | 1.41 |
| 0.1 | 1.288 | 1.30 | 1.115 | 1.208 | 1.28 | 1.36 |
| 0.3 | 1.279 | 1.29 | 1.096 | 1.185 | — | — |
| 0.5 | 1.270 | 1.28 | 1.087 | 1.171 | — | — |
| 1.0 | 1.257 | 1.26 | 1.070 | 1.154 | — | — |
| 2.0 | 1.240 | 1.24 | — | — | — | — |
| 3.0 | 1.222 | 1.22 | — | — | — | — |
| 5.0 | — | 1.19 | — | — | — | — |

SUMMARY.

The redox potentials of the ruthenium II complexes with substituted derivatives of 2:2' dipyridyl and o-phenanthroline have been determined, and a redetermination of the potentials of the complexes with the parent bases have been made. Methyl groups in both bases depress the potential, whilst the potential of the complex with 5-bromo-o-phenanthroline is the highest of all. The ruthenium compounds thus follow the same trend as the ferrous compounds. At equivalent acid concentrations, the redox potentials of tris-o-phenanthroline ruthenium salts is always higher than of the tris-2:2' dipyridyl analogues.

ACKNOWLEDGEMENTS.

The author is indebted to the Research Committee, University of Sydney, for a grant for the purchase of ruthenium ; and to Miss J. Fildes for micro-analysis of the compounds.

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THE CHEMISTRY OF RUTHENIUM.

PART IV. THE POTENTIAL OF THE QUADRIVALENT/TRIVALENT RUTHENIUM COUPLE IN HYDROCHLORIC AND HYDROBROMIC ACIDS.

By J. R. BACKHOUSE, M.Sc.,
and F. P. DWYER, D.Sc.

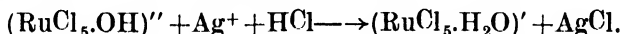
Manuscript received, August 8, 1949. Read, September 7, 1949.

Grube and Fromm (1941) investigated the potential of the quadrivalent/trivalent ruthenium couple in a limited range of hydrochloric acid concentrations, and found that it varied from 0.858 volt in 2 normal acid to 0.908 volt in 0.5 normal acid. It was concluded that the reaction was not the simple $\text{Ru}^{4+} + e' \rightarrow \text{Ru}^{3+}$; but hydrogen and chloride ions were also involved. A study of the quadrivalent/trivalent osmium couple in hydrobromic acid (Dwyer, McKenzie and Nyholm, 1946) and in hydrochloric acid (Dwyer, Humpoletz and Nyholm, 1947a) showed that whilst the potentials in hydrobromic acid were usually much lower, when the acid concentrations became small, they coincided. From this observation and the shapes of the curves it was concluded that the reaction measured in low acid concentrations was $\text{OsO}^{++} + e' \rightarrow \text{OsO}^{+}$.

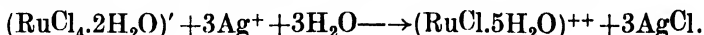
The quadrivalent/trivalent ruthenium couple has now been investigated over a wide range of acid concentrations of hydrochloric and hydrobromic acids in order to determine whether a similar reaction might not apply.

As with quadrivalent osmium, simple salts of quadrivalent ruthenium do not exist. The complex hexahalogenates R_2RuX_6 ($\text{X} = \text{Cl}, \text{Br}$), the analogues of the osmium complexes used, are decomposed even in strongly acid solutions, and the hydroxypentahalogenates, $\text{R}_2(\text{RuX}_5\text{OH})$ result. It is probable that in very dilute acid further replacement of the halogen by hydroxyl may result, but definite compounds have not been isolated.

Trivalent ruthenium is normally obtained by treatment of the quadrivalent compounds with alcohol, sulphurous acid, or stannous chloride, or by cathodic reduction. The present authors have found silver wool especially satisfactory, as the silver halide is precipitated and easily removed.

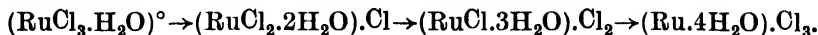


Two series of complex salts result, $\text{R}(\text{RuCl}_4\cdot 2\text{H}_2\text{O})$, of which the free acid $\text{H}(\text{RuCl}_4\cdot 2\text{H}_2\text{O})$ has been isolated in green *cis* and red *trans* forms (Charonnat, 1931), and the pentahalogeno-aquo complexes, $\text{R}_2(\text{RuCl}_5\text{H}_2\text{O})$ (Charonnat, *loc. cit.*; Howe, 1927). In both compounds the molecules of water are firmly bound, whilst Buividate (1935), operating with the ammonium salt of the red series, found that excess of silver nitrate would precipitate only three of the four halogen atoms. The reaction involved was probably



However, Grube and Nann (1939), by evaporating a solution of ruthenium trichloride over concentrated sulphuric acid in high vacuum, or in a current of dry hydrochloric acid at high temperatures isolated the monohydrate, $\text{RuCl}_3\cdot \text{H}_2\text{O}$, which they concluded demonstrated the tetravalency of ruthenium III. It was suggested that when solutions of this substance in dilute hydrochloric acid

were allowed to stand successive additions of aquo groups took place according to the scheme



From conductivity experiments and titration with silver nitrate it was found that the first compound contained no ionisable halogen, but on standing not much more than one chlorine atom was ionised, so that the last stage of the scheme is very doubtful. It is difficult to reconcile the conflicting data of Buividate and Grube and Nann on this point, but it may be concluded that at least one chlorine atom is non-ionisable in ruthenium trichloride, and very probably two, since Buividate used an excess of silver nitrate.

Grube and Fromm (1940) also claimed the existence of the diaquo compound above in *cis* and *trans* forms. This claim was made on the observation that greenish solutions of the compound on standing became brown without any increase in the conductivity or precipitable halogen. There is a multitude of evidence, however, for the preferred hexacovalency of trivalent ruthenium (Charonnat, *loc. cit.*; Morgan and Burstall, 1936; Werner and Smirnov, 1920; Dwyer, Humpoletz and Nyholm, 1947*b*), and these various aquo salts, if they exist, should thus be formulated as are the aque chromium III chlorides. The alleged green isomer is thus the *cis* form of the octahedral complex $[\text{RuCl}_2 \cdot 4\text{H}_2\text{O}]^+$, or alternatively due to traces of blue ruthenium II salts obtained by carrying the reduction too far.

In this study, the oxidising solution of the hydroxypentahalogeno ruthenate IV was made up to a specified volume by the addition of acid or various salts, and distilled water and freed from oxygen by the passage of carbon dioxide. The reductant solution was made from a fresh portion of the oxygen-free oxidant solution by reduction with silver wool in an atmosphere of carbon dioxide. After mixing, the equimolar solution of oxidiser and reducer was allowed to reach equilibrium among the various ions for two weeks. During this period the potential usually fell slightly, indicating that oxidation of the ruthenium III had not occurred. The potential was measured with two independent electrodes of gold and smooth platinum, which at equilibrium gave the same potential within 0.2 millivolt. The system was badly "poised", and measurement with the ordinary potentiometer was not possible; but with a valve potentiometer steady reproducible potentials were obtained.

In the presence of hydrochloric acid the potential of the system (using potassium pentachlorohydroxy ruthenate IV as the oxidant) rose rapidly, reaching a maximum at about 0.3 N acid and then decreased sharply (Table I, Curve I). The initial sharp rise in the potential can be ascribed to the reversal of the hydrolysis of the oxidant ion, since the addition of neutral salts such as ammonium sulphate to the weakly acid solution precipitated the colloidal black ruthenium dioxide. The subsequent decrease in the potential leads to the conclusion that the ionic species present in the dilute acid are chiefly cations which are gradually transformed into complex ions.

In the presence of hydrobromic acid (using potassium pentabromohydroxy ruthenate IV as the oxidant), the potential showed also a sharp rise, followed by a marked decrease. However, the potential was always much lower than in the chloride system (Table II, Curve II). It can be concluded, therefore, that unlike the osmium III/osmium IV system, different ionic species exist in the two acids, and that halogen is bound to the metal. The lower potential in hydrobromic acid is consistent with the more pronounced covalent bonding of the bromine atom.

Conclusive evidence for the pronounced effect of the halogen ion on the potential in the chloride system was obtained by a series of measurements, in which the effects of hydrogen ion, chloride ion and ionic strength were studied

TABLE I.
The Effect of Hydrochloric Acid on the Ru^{IV}/Ru^{III} Potential.
 (Cf. Curve I, Fig. 1.)

| Acid Concentration. Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|--------------------------------------|-------------------------|-----------------------------|
| 0.2 | 0.674 | 0.918 |
| 0.25 | 0.688 | 0.932 |
| 0.325 | 0.678 | 0.922 |
| 0.423 | 0.675 | 0.919 |
| 0.596 | 0.661 | 0.905 |
| 0.77 | 0.649 | 0.893 |
| 0.94 | 0.637 | 0.881 |
| 1.46 | 0.608 | 0.852 |
| 2.5 | 0.557 | 0.801 |
| 3.53 | 0.520 | 0.764 |
| 4.57 | 0.490 | 0.734 |
| 5.47 | 0.470 | 0.714 |

TABLE II.
The Effect of Hydrobromic Acid on the Ru^{IV}/Ru^{III} Potential.
 (Cf. Curve II, Fig. 1.)

| Acid Concentration. Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|--------------------------------------|-------------------------|-----------------------------|
| 0.2 | 0.491 | 0.735 |
| 0.25 | 0.531 | 0.775 |
| 0.472 | 0.503 | 0.747 |
| 0.916 | 0.480 | 0.724 |
| 2.03 | 0.436 | 0.680 |
| 3.58 | 0.395 | 0.639 |
| 4.25 | 0.380 | 0.624 |
| 6.02 | 0.357 | 0.601 |
| 6.91 | 0.340 | 0.584 |

separately. With fixed chloride ion concentrations of 0.025 N and 1.115 N the hydrogen ion concentration was increased by means of sulphuric acid (Tables III, IV, Curves III, IV). In each series the potential decreased with increasing hydrogen ion concentration, but the decrease was much smaller than with hydrochloric acid. When the hydrogen ion concentration was kept constant at 0.25 N and 1.115 N in the next series of measurements and the chloride ion concentration increased with potassium chloride, the potential decreased sharply, the curves being only slightly higher than the hydrochloric acid curve (Tables V, VI, Curves V, VI). The increase in ionic strength was made at fixed hydrogen and chloride ion concentrations by the addition of ammonium sulphate. The decrease in the potential was relatively small (Table VII).

The decrease in the potential of a redox system by the addition of neutral salts can usually be ascribed either to the disproportionate reduction of the activity of the oxidiser, by reason of its greater charge in cationic systems (such as the ferric/ferrous system), or to complex ion formation with the oxidiser. In an anionic system involving complex metallic ions, the reductant usually carries the greater charge as in the ferricyanide/ferrocyanide system (Kolthoff

TABLE III.

*The Effect of Hydrogen Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Chloride Ion Concentration, 0.25 N.
(Cf. Fig. 2, Curve III.)*

| Total Hydrogen Ion Concentration Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|---|-------------------------|-----------------------------|
| 0.25 | 0.688 | 0.932 |
| 0.505 | 0.701 | 0.945 |
| 0.76 | 0.699 | 0.943 |
| 1.015 | 0.699 | 0.943 |
| 1.52 | 0.693 | 0.937 |
| 2.54 | 0.680 | 0.924 |
| 3.65 | 0.671 | 0.915 |
| 4.36 | 0.660 | 0.904 |
| 6.63 | 0.612 | 0.856 |

TABLE IV.

*The Effect of Hydrogen Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Chloride Ion Concentration, ---5 N.
(Cf. Fig. 2, Curve IV.)*

| Total Hydrogen Ion Concentration Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|---|-------------------------|-----------------------------|
| 1.115 | 0.629 | 0.873 |
| 2.135 | 0.617 | 0.861 |
| 3.155 | 0.602 | 0.846 |
| 4.17 | 0.584 | 0.838 |
| 6.22 | 0.557 | 0.803 |

TABLE V.

*The Effect of Chloride Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Hydrogen Ion Concentration, 0.25 N.
(Cf. Fig. 2, Curve V.)*

| Total Chloride Ion Concentration, Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|--|-------------------------|-----------------------------|
| 0.25 | 0.688 | 0.932 |
| 0.425 | 0.695 | 0.939 |
| 0.687 | 0.671 | 0.915 |
| 1.125 | 0.646 | 0.890 |
| 1.65 | 0.620 | 0.864 |
| 2.26 | 0.598 | 0.842 |

and Tomsicek, 1935) and the chloriridate/chloriridite and bromiridate/bromiridite systems (Dwyer, McKenzie and Nyholm, 1944, 1947c). As a result, the potential rises with increasing ionic strength. It is evident that in determining the constitution of a redox system the effects of both complex ion formation and the ionic strength must be considered.

TABLE VI.

*The Effect of Chloride Ion Concentration on the Ru^{IV}/Ru^{III} Potential.
Hydrogen Ion Concentration, 1.115 N.
(Cf. Fig. 2, Curve VI.)*

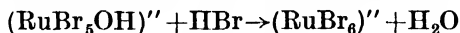
| Total Chloride Ion Concentration, Normality. | E, Observed. (Volt.) | E _h . (Volt.) |
|--|----------------------|--------------------------|
| 1.115 | 0.629 | 0.873 |
| 1.64 | 0.602 | 0.846 |
| 2.17 | 0.580 | 0.824 |
| 3.13 | 0.556 | 0.800 |

TABLE VII.

The Effect of Ammonium Sulphate on the Ru^{IV}/Ru^{III} Potential.

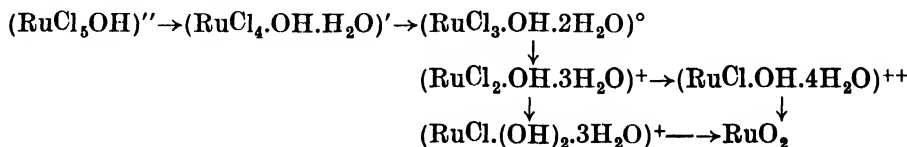
| Hydrochloric Acid Concentration Normality. | E _h . (Volt.) | Total Normality with Ammonium Sulphate. | E _h . (Volt.) |
|--|--------------------------|---|--------------------------|
| 0.77 | 0.893 | 1.27 | 0.889 |
| 0.94 | 0.881 | 2.45 | 0.869 |
| 1.46 | 0.852 | 3.98 | 0.839 |

It can be assumed from general principles that the reductant is the more cationic, and from the observations of Ruivodate and Grube and Nann (*loc. cit.*) it is probable that the ion present in dilute solution is the hydrated (RuX₂)⁺ or less, probably (RuX)⁺⁺. With increasing halogen ion concentration there will be a tendency for the formation of complex anions such as (RuX₄.2H₂O)' and (RuX₅.H₂O)'', but the stability of such ions, if the usual rule is followed, will be much smaller than similar complex anions formed by the oxidant, and their effect can thus be neglected. The separation of black ruthenium dioxide from solutions of potassium pentachlorohydroxy ruthenate IV in very dilute acid leads to the conclusion that this salt can undergo progressive dissociation. Observations on the colour of solutions of the bromo compound in various concentrations of hydrobromic acid supports this view. Thus the deep purple colour in normal hydrobromic acid gradually becomes lighter and brownish in colour-like dilute solutions of the chloro compound—as the acid is diluted and finally darkens with the separation of ruthenium dioxide. If the acid concentration is raised above 3.5 normal, the purple colour changes to brown, suggesting the replacement of the hydroxyl group by bromine has occurred.



This latter reaction cannot be performed on the chloro compound with even concentrated hydrochloric acid.

The progressive dissociation of the chloro compound can be expected to follow a scheme such as



The dissociation of the initial compound can be repressed by direct replacement of aquo and hydroxyl groups by chloride ions, the latter replacement being facilitated by hydrogen ions.

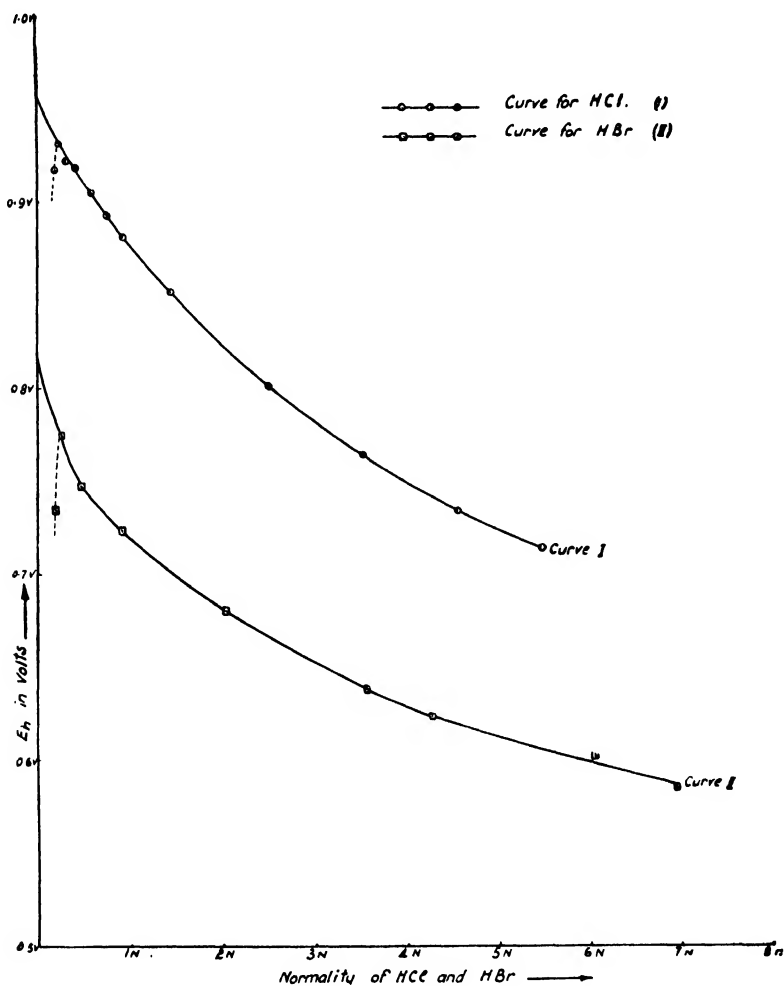
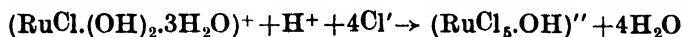
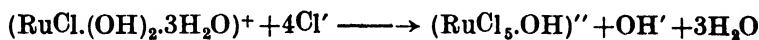
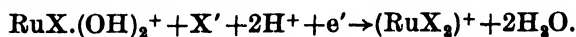


Fig. 1.

It is considered that the potential measured in dilute acid at the point where the maximum is reached is of the reaction



The potential extrapolated from this point to zero acid concentration, for the chloride system was 0.96 ± 0.002 volt, and for the bromo system 0.82 ± 0.002 volt.

EXPERIMENTAL.

Oxidant and Reductant Solutions.

Potassium pentachlorohydroxy ruthenate IV was prepared by the method of Charonnat (*loc. cit.*) from the pure metal. The purplish brown crystals were recrystallised from normal hydrochloric acid, and dried in vacuum over sulphuric acid. The oxidant solution was made in oxygen-free normal hydrochloric acid, and was M/100. Solutions in 0.1 N acid darkened slightly on keeping, but in 0.20 N acid ruthenium dioxide gradually precipitated.

(b) *Potassium aquopentachloro ruthenate III* was prepared by taking a portion of the oxidant solution above, and allowing it to stand in an atmosphere of carbon dioxide in contact with silver

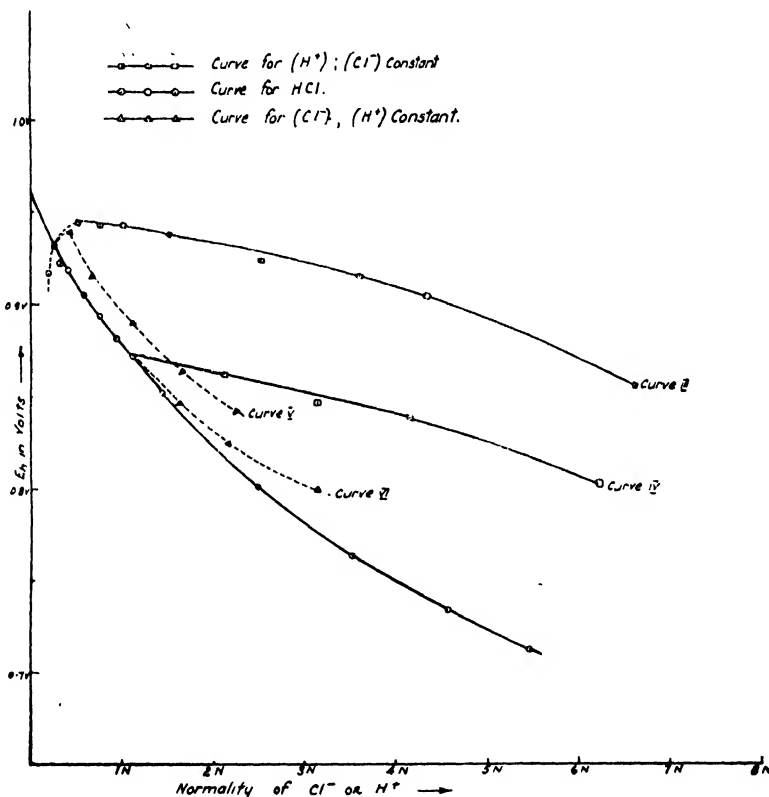


Fig. 2.

wool. At the end of twenty-four hours, the colour had changed to yellow, and the precipitate of the silver halide had settled out. No trace of ruthenium metal was formed during the reduction. The reduced solution was kept over silver wool in the inert atmosphere.

(c) *Potassium pentabromohydroxy ruthenate IV*. This substance was prepared by the same method as the chloro compound, either by treatment of the potassium ruthenate with hydrobromic acid, or by fusion of ruthenium metal with potassium hydroxide and potassium bromate, followed by extraction with water and treatment with hydrobromic acid. The dark purplish brown crystals were recrystallised from dilute hydrobromic acid. The M/100 solution was made in normal hydrobromic acid.

(d) *Potassium aquopentabromo ruthenate III*. The reduction of the purple oxidant solution could not be performed with alcohol in the presence of hydrobromic acid, whilst in the absence of acid or in very dilute acid, hydrolysis caused the deposition of some ruthenium dioxide.

Reduction with silver wool gave the required pale yellow solution of the compound, but the reduction tended to form some bivalent ruthenium compound owing to the low potential of the reaction $\text{Ag} + \text{Br}^- \rightarrow \text{AgBr} + e^-$. However it was found that the colour change from yellow to the pale green of the ruthenium II compound was quite sharp, and thus by the addition of some of the oxidant solution it was possible to remove the bivalent state. The solution was stored in an atmosphere of carbon dioxide.

Apparatus. The redox assembly, with a saturated potassium chloride salt bridge, was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1944). The potential of the saturated calomel electrode was taken as 0.2443 volt at 25° C. The potentials on gold and platinum electrodes were measured on a Leeds and Northrup valve potentiometer, and are considered accurate to $\pm 2\text{mv}$.

Procedure. The oxidant solution (5 ml.) was mixed with acid, and distilled water in that order to prevent hydrolysis and made up to 35 ml. Where potassium chloride and ammonium sulphate were added, the dry salts were used, and dissolved at room temperature. The hydrobromic acid was freshly distilled, free from bromine, and was stored over carbon dioxide. The prepared solution was freed from traces of air by passage of carbon dioxide and the reductant solution (5 ml.) added. The final mixture was thus M/800 with respect to both oxidant and reductant. It was allowed to stand in an inert atmosphere for two weeks. When equilibrium had been established among the various ions, the mixture was placed in the redox vessel, previously filled with carbon dioxide, and allowed to come to equilibrium with the electrodes. During this time—usually 24 hours—the potential decreased slightly. Finally the salt bridge was inserted, and the equilibrium potential measured whilst the solution was stirred with a current of carbon dioxide. The results of the various measurements are shown in the foregoing tables and curves.

SUMMARY.

The potential of the quadrivalent/trivalent ruthenium couple has been studied in hydrochloric and hydrobromic acid solutions. From the shapes of the curves it is concluded that the system is cationic. The potential is depressed markedly by halide ions and to a lesser extent by hydrogen ions. The results are consistent with the existence of hydrated cations of the type $(\text{RuX}(\text{OH})_2)^+$ and $(\text{RuX}(\text{OH}))^{++}$ for the oxidant and $(\text{RuX}_2)^+$ and $(\text{RuX})^{++}$ for the reductant. The potentials for the chloro and bromo systems respectively, extrapolated from the point where hydrolysis becomes serious to zero acid concentrations are 0.96 ± 0.002 volt and 0.82 ± 0.002 volt.

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PART III

THE CHEMISTRY OF RUTHENIUM.

PART V. THE POTENTIAL OF THE BIVALENT/TRIVALENT RUTHENIUM COUPLE IN HYDROCHLORIC ACID.

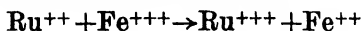
By J. R. BACKHOUSE, M.Sc.,
and F. P. DWYER, D.Sc.

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When a solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid is treated with strong reducing agents such as zinc or lead, the deep brown colour changes successively to yellow, green, blue, and finally deposits the metal itself. The yellow solution contains trivalent ruthenium (Howe, 1927; Charonnat, 1931), but for a time a controversy existed over the green and blue substances, which were thought to contain respectively bivalent and monovalent ruthenium. According to Latimer (1940) the question has been definitely settled by the work of Crowell and Yost (1928), who showed that the blue solution contained the element in the bivalent state, whilst the green colour was due to a mixture of the trivalent and bivalent states. Recently, however, Grube and Nann (1939), as a result of the study of the electrolytic reduction of ruthenium trichloride in hydrochloric acid, claimed that the reduction proceeded to the bivalent state in concentrated acid, but in dilute acid the univalent state resulted. The reduction steps were identified by potentiometric titration with hydrogen peroxide. Univalent ruthenium was found to undergo disproportionation— $2\text{Ru}^+ \rightarrow \text{Ru}^{++} + \text{Ru}$; and the potential of the reaction $\text{Ru}^+ - e' \rightarrow \text{Ru}^{++}$ was found to be in the range 0.03 to 0.05 volt. The published titration curves, however, do not show well-marked inflexions; the potentials from which the curves were obtained were almost instantaneous and not equilibrium values, and an irreversible oxidant was used. Additional evidence in substantiation of univalent ruthenium is therefore desirable.

The present investigation deals with the determination of the potential of the bivalent/trivalent ruthenium couple in hydrochloric acid with a view to checking the existence of the univalent state.

The mixed oxidant/reductant solution was prepared by the reduction of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid with pure lead foil in an oxygen-free atmosphere of carbon dioxide. The resulting deep blue solution contained 15–20% of bivalent ruthenium, whilst the remainder was trivalent. Although the lack of equimolarity in this solution involved a large correction to obtain the standard potential, the large excess of the trivalent state automatically eliminated the possibility of any of the alleged monovalent state being present. The reduced solution to which varying amounts of acid were added was allowed to come to equilibrium with a smooth gold electrode in an atmosphere of carbon dioxide. As soon as the potential reading was taken the concentration of bivalent ruthenium was determined by addition of a known volume of the solution to oxygen-free ferric alum solution. In this way an equivalent amount of ferrous salt was formed.



From the present work it is known that the potential of the $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ system is of the order of 0.1 volt, whilst from the previous paper (This Series,

Part III) the potential of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{IV}}$ system is approximately 0.9 volt, hence the ferric salt can only oxidise to the trivalent state. The partly reduced iron solution was then oxidised potentiometrically with potassium permanganate, the first step being due to oxidation of the ferrous ion. The total ruthenium in the solution was estimated by oxidation to the quadrivalent state with a slight excess of chlorine, followed by potentiometric titration with stannous chloride. The potential of the stannous/stannic system (0.13 volt; Latimer, 1940) is such that the reduction $2\text{Ru}^{4+} + \text{Sn}^{++} \rightarrow 2\text{Ru}^{3+} + \text{Sn}^{4+}$ proceeds to completion without the formation of any bivalent ruthenium compound, or the separation of ruthenium metal. The difference in the total ruthenium concentration and the bivalent ruthenium concentration then gives the concentration of trivalent ruthenium.

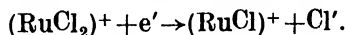
The observed potentials were corrected to the standard equimolar potential by the usual equation. Since the activities of the oxidant and reductant were unknown, the observed concentrations were substituted.

The reduction of ruthenium tribromide in hydrobromic acid could be effected with either silver or lead, but the reduced solution was coloured green. Even when the reduction was carried out with zinc to the point where most of the metal was deposited, the colour remained green. It was concluded that the green colour was not due to admixture of the bivalent and trivalent states, but that the ionic species of bivalent ruthenium is not the simple hydrated Ru^{++} but hydrated $(\text{RuBr})^+$ and $(\text{RuCl})^+$. The determination of the potential of the green solution was not successful as a brown deposit formed on the electrode, whilst a satisfactory method could not be found for the estimation of the bivalent ruthenium. The potential of the trivalent/quadrivalent ruthenium couple in hydrobromic acid (approx. 0.7 volt) is almost the same as the ferrous ferric system. The reaction $\text{Ru}^{++} + \text{Fe}(\text{CN})_6''' \rightarrow \text{Ru}^{3+} + \text{Fe}(\text{CN})_6''''$, although theoretically feasible, proved to be unsuitable.

The potential of the chloride system was found to be almost independent of the acid concentration from 1.5 N to 6.8 N hydrochloric acid. Measurements in the lower acid concentrations could not be obtained owing to the separation of ruthenium on the electrode



From the independence of the potential on the ionic strength, it can be concluded that increasing ionic strength has the same effect on the activities of both the oxidant and the reductant, and hence that they probably carry the same charge. Since the lowest valencies of the metal are involved, the system is almost certainly cationic, and the equivalence of charge must be due to covalent bonding of part of the halogen. In Part III of this series evidence was put forward for the existence of ruthenium trichloride in dilute solution as either the hydrated ion $(\text{RuCl})^{++}$ or $(\text{RuCl}_2)^+$, and from the behaviour of ruthenium tribromide towards reducing agents it is suggested that the reductant ion is $(\text{RuCl})^+$. It is considered, therefore, that the redox reaction of the couple is



The potential of the trivalent/bivalent couple in 1.53 N acid, 0.084 volt is not very much higher than the potential of the alleged bivalent/monovalent couple measured by Grube and Nann (*loc. cit.*)—0.03 to 0.05 volt in 0.1 N acid. In solution containing small concentrations of hydrochloric acid, ruthenium trichloride is known to hydrolyse extensively (Grube and Fromm, 1940). As a result the potential of the Ru^3/Ru^2 system can be expected to be quite low in low concentrations of hydrochloric acid. It is also significant that the disproportionation, which was supposed to be due to univalent ruthenium, occurs with bivalent ruthenium in weakly acid solution. This could well arise by dissociation of the $(\text{RuCl})^+$ ion to Ru^{++} , which undergoes disproportionation.

It is concluded from the present study that the univalent ruthenium ion has no existence in solution.

EXPERIMENTAL.

Oxidant and Reductant Solutions.

An M/50 solution of potassium pentachlorohydroxy ruthenate IV in hydrochloric acid (2 N) was saturated with oxygen-free carbon dioxide and thin strips of lead foil added. After about thirty minutes the deep brown solution had become yellow and the reaction had almost stopped by the deposition of ruthenium on the lead. The solution was decanted on to fresh lead, and sealed in carbon dioxide until after 20–30 minutes a deep royal blue solution had formed. This was filtered from lead chloride and ruthenium metal through a sintered glass filter into a storage vessel, fitted with a burette, so that known volumes could be withdrawn without exposure to oxygen. Since the acid concentration had changed during the reduction by reaction with the lead, the acidity was determined by titration with sodium hydroxide and methyl orange indicator. The total ruthenium in the solution was estimated by dilution of a known volume with dilute hydrochloric acid and oxidation with a slight excess of chlorine water. The excess was then boiled out, and the solution potentiometrically titrated with standard stannous chloride. The excess of chlorine was such that any loss as ruthenium tetroxide could be regarded as negligible. The solution was found to be M/800 with respect to ruthenium.

Apparatus.

The redox apparatus was the same as that used in previous determinations (Dwyer, McKenzie and Nyholm, 1946). The saturated calomel electrode, taken as 0.2443 volt at 25° C., was connected to the cell through a saturated potassium chloride salt bridge. During the potential determinations the apparatus was sealed with apeizon wax and kept under a slight pressure of carbon dioxide.

Procedure.

An oxygen-free solution (30 ml.) of hydrochloric acid of the required concentration was saturated with carbon dioxide in the redox vessel, the reduced ruthenium solution (10 ml.) added quickly, and the apparatus sealed. After approximately 24 hours equilibrium had been attained, and the potential was measured with a Leeds and Northrup valve potentiometer. The system was unpoised and the ordinary potentiometer was unreliable. A portion of the solution (30 ml.) was immediately withdrawn through a stream of carbon dioxide and added to oxygen-free standard ferric alum solution. Potentiometric titration with potassium permanganate then gave the concentration of bivalent ruthenium at the equilibrium point.

The potential values at the various acid concentrations are shown in Table I.

TABLE I.
The Potential of the Ru^{II}/Ru^{III} System in Hydrochloric Acid.
Total Ru Concentration, 1.25×10^{-3} M.

| Acid Concentration Normality. | E, Observed. (Volt.) | [Ru ⁺⁺] $\times 10^{-3}$ | [Ru ⁺⁺⁺] $\times 10^{-3}$ | E, Observed Corrected. (Volt.) | E _h . (Volt.) |
|-------------------------------|----------------------|--------------------------------------|---------------------------------------|--------------------------------|--------------------------|
| 1.53 | —0.128 | 0.279 | 0.97 | —0.160 | 0.084 |
| 2.6 | —0.130 | 0.301 | 0.95 | —0.160 | 0.084 |
| 2.6 | —0.132 | 0.305 | 0.945 | —0.161 | 0.083 |
| 3.64 | —0.121 | 0.27 | 0.98 | —0.154 | 0.090 |
| 5.22 | —0.131 | 0.27 | 0.98 | —0.164 | 0.080 |
| 6.8 | —0.127 | 0.28 | 0.97 | —0.157 | 0.087 |

SUMMARY.

The potential of the bivalent/trivalent ruthenium couple in hydrochloric acid was found to be $0.084 \text{ volt} \pm 0.005 \text{ volt}$ in the hydrochloric acid range of concentrations from 1.53 N to 6.8 N. It is considered that the system is cationic with the ionic species $(\text{RuCl}_2)^+$ and $(\text{RuCl})^+$ for the oxidant and reductant respectively. From the potential values and the behaviour of the system in low acid concentrations, it is concluded that Grube and Nann's alleged univalent ruthenium is really bivalent ruthenium.

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KEPLER'S PROBLEM.

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Abstract.—Kepler's problem is reviewed from analytical and numerical standpoints, the region of usefulness of various solutions defined and formulae suggested for the nearly parabolic case. A bibliography is given.

The two body problem was solved (kinematically) by Kepler with the enunciation of his three laws of planetary motion which were later to be contained within the implications of the more general theory of gravitation. The Keplerian rules (regarded as derived from the gravitational equations) are still used in most derivations of the equations which connect the position variables of planetary motion with the time variable. The problem of finding the coordinates of a planet in the plane of its orbit in unperturbed motion is Kepler's problem.

If we express the equation of the solution path of planetary motion in a form using the parameters e (eccentricity) and q (perihelion distance) which apply equally to the three conics without involving infinite or imaginary values (as for example the major and minor axes would) and take x_0, y_0 as the rectangular coordinates in the plane of motion with the x_0 axis directed towards perihelion we obtain

$$x_0^2 + y_0^2 = \{q(1+e) - ex_0\}^2 \quad (1)$$

The equation for constancy of areal velocity is

$$x_0 y_0' - x_0' y_0 = c$$

that is

$$2x_0 y_0' - (x_0 y_0)' = c$$

where the dashes indicate differentiation with regard to time.

Now if we write

$$\lambda = \frac{x_0}{q}, \quad \mu = \frac{y_0}{q} \quad \text{and} \quad \varepsilon = \frac{1-e}{1+e} \quad (2)$$

and take the initial point at perihelion this becomes

$$\int_0^{\mu_1} 2q^2 \lambda d\mu - q^2 \lambda_1 \mu_1 = ct \quad (3)$$

and equation (1) gives

$$\lambda = \frac{1}{1-e} \{-e \pm (1 - \varepsilon \mu^2)^{\frac{1}{2}}\} \quad (4)$$

In substituting (4) into (3) in the elliptic case the branch of λ corresponding to the upper sign must be used from perihelion ($\mu=0, \lambda=1$) to $\mu=\varepsilon^{-\frac{1}{2}}, \lambda=-e/(1-e)$ and that corresponding to the lower sign from this point to $\mu=0, \lambda=-\varepsilon^{-1}$. In the hyperbolic case the lower sign corresponds to the non-solution branch of the hyperbola. The case $e=1$ is obvious.

On integrating (3) in this way, putting $c=kq^{\frac{1}{2}}(1+e)^{\frac{1}{2}}$ from the dynamical theory where k is the Gaussian constant, we obtain

$$k(1+e)^{\frac{3}{2}} q^{-\frac{3}{2}} t = \varepsilon^{-\frac{3}{2}} \{ \pm \sin^{-1} \varepsilon^{\frac{1}{2}} \mu - e \varepsilon^{\frac{1}{2}} \mu \} + C \quad (5)$$

where the subscript on μ may now be dropped without ambiguity. In the elliptic case we can without loss of generality take the positive sign and $C=0$ if we put $\sin^{-1}\epsilon^{1/2}\mu > \pi/2$ in the interval in which μ is decreasing. The hyperbolic case requires only the upper sign.

From (4) we obtain

$$\lambda = 1 - \frac{\mu^2}{1+e} \frac{1 \mp (1-\epsilon\mu^2)^{1/2}}{\epsilon\mu^2}, \quad (6)$$

with the same remarks about signs. This will be found a convenient form for calculation.

Equation (5) will be taken as the general expression of Keplerian motion. If we put $\epsilon^{1/2}\mu = \sin E$

$$M = ka^{-3/2}t = E - e \sin E, \quad (7)$$

where a is the semi-major axis, M the mean anomaly and E the eccentric anomaly.

When ϵ is negative put $\epsilon = -\alpha = (e-1)/(e+1)$, $\sinh F = \alpha^{1/2}\mu$ and we obtain (since $\sin^{-1}i\alpha^{1/2}\mu = i \sinh^{-1}\alpha^{1/2}\mu$)

$$M = ka^{-3/2}t = e \sinh F - F. \quad (8)$$

Equation (5) may be written

$$D = 12k(1+e)^{1/2}q^{-3/2}t = 12\mu + \mu^3(1+\epsilon)6 \left(\frac{\sin^{-1} \epsilon^{1/2}\mu - \epsilon^{1/2}\mu}{\epsilon^{3/2}\mu^3} \right), \quad (9)$$

which will be found a convenient expression for dealing with the nearly parabolic case (e near 1).

For the parabolic case ($e=1$)

$$12\sqrt{2}kq^{-3/2}t = 12\mu + \mu^3 \quad (10)$$

and if we place

$$\tan \frac{v}{2} = \tau = \frac{1}{2}\mu$$

we obtain

$$6k(2q)^{-3/2}t = 3\tau + \tau^3$$

which is the usual expression for parabolic motion, where v is the true anomaly.

Equation (7) is the one which now bears Kepler's name. It is an early example of a transcendental equation occurring in applied mathematics and very few men even as eminent as Kepler can have such an enduring memorial as this equation. The necessity for its frequent solution and the difficulties, numerical and analytical, which it presents have kept alive interest in the equation during the whole of the 300 years since its discovery. The analytical points involved if we wish to express the implicit function E of equation (7) explicitly as a series in M and e are of interest and consideration of them has been important in the development of the theory of analytic functions (see references in Wintner, 1941). The interval of convergence as a power series in e must depend on the singularities of the function $E=E(e, M)$ in the complex plane for e .

The function

$$e = \frac{E-M}{\sin E} \quad (11)$$

is a meromorphic function with simple poles at the points $\sin E=0$ except when $E=M$.

The inverse function $E=E(e, M)$ must be multiple valued and the branch for which $e=0$ implies $E=M$, that is the branch in which we are interested,

is regular at $e=0$. The singularities of the inverse function are given by zeros of the derivative, that is by

$$\frac{1-e \cos E}{\sin E}=0$$

The singularities at $E=\infty$ correspond to connected paths to infinity (see Hurwitz, 1906) in the E plane for which e , given by (11), approaches a finite point. This only occurs for $e=0$ and therefore does not affect the branch in which we are interested, which is regular at this point. Hence the singularities are determined by (11) and the equation

$$M-E+\tan E=0 \quad (12)$$

where M is real (in the elliptical case).

Every point on the real axis of e for which $|e| > 1$ is a branch point. Let us put $E=a+ib$ into equation (12) and equate real and imaginary parts giving

$$b = \frac{(1+\tan^2 a) \tanh b}{1+\tan^2 a \tanh^2 b}, \quad (13)$$

$$-M+a = \frac{(1-\tanh^2 b) \tan a}{1+\tan^2 a \tanh^2 b},$$

from which

$$\tan^2 a = \frac{\tanh b - b}{(b \tanh b - 1) \tanh b} \quad (14)$$

and

$$(a-M)^2 = (\tanh b - b)(b - \coth b) \quad (15)$$

Equation (15) shows that b must lie between $-\beta$ and $+\beta$ where β is given by

$$\beta = \coth \beta$$

If, using equations (11) and (12), we write

$$\xi + i\eta = e = \sec E,$$

equate real and imaginary parts and use equation (13) we obtain

$$\left. \begin{aligned} \xi &= b \cos a \operatorname{cosech} b, \\ \eta &= b \sin a \operatorname{sech} b. \end{aligned} \right\} \quad (16)$$

If we now use b as a parameter equations (14) and (16) give the curve of singularities.

For the case of the hyperbola M is replaced by iN (with N real); equation (12) becomes

$$-iN + E - \tan E = 0$$

and any real value of e for which $|e| < 1$ gives a solution (that is a singularity).

If as before we let $E=a+ib$, $e=\xi+i\eta$ the equations corresponding to (14), (15) and (16) are

$$\left. \begin{aligned} \tanh^2 b &= \frac{\tan a - a}{(1+\tan a) \tan a}, \\ (b-N)^2 &= (\tan a - a)(\cot a + a) \end{aligned} \right\} \quad (17)$$

and

$$\left. \begin{aligned} \xi &= (b-N) \cos a \operatorname{cosech} b, \\ \eta &= (b-N) \sin a \operatorname{sech} b. \end{aligned} \right\} \quad (18)$$

The curves (symmetrical about both axes) of singularities for the ellipse and the hyperbola are shown in Figure 1, where the dashed line refers to the

ellipse and the dotted line to the hyperbola. The curve for the ellipse was first discussed by T. Levi-Civita (1904a) and C. V. L. Charlier (1904) (the work of the latter not having been available to me) and the hyperbola by H. G. Block (1904). Other discussions are given by H. Andoyer (1923) and A. Wintner (1941).

For elliptic motion the nearest singular point to the origin is on the imaginary axis at a point given by

$$\beta = \coth \beta$$

$$\eta = \beta \operatorname{sech} \beta = 0.6627 \dots$$

The power series expression for E in elliptic motion is convergent uniformly with M only for $0 \leq e < 0.6627 \dots$. In both cases the curve is incident with real axis at an angle of $\pi/3$ and in the hyperbolic case the curve is asymptotic to the line $\xi = \pi/2$.

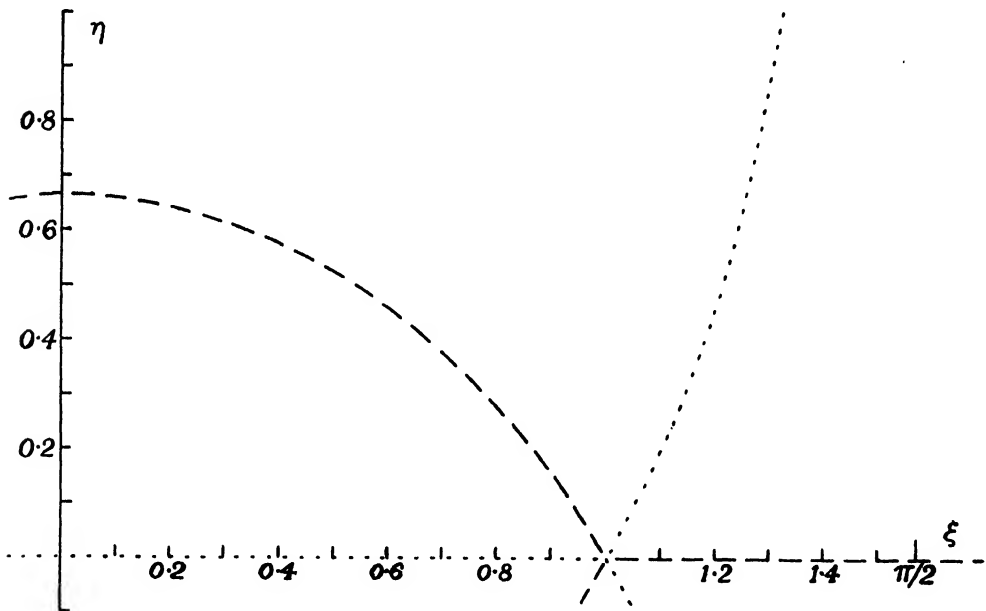


Fig. 1.—Curves of singularities in the complex e plane (first quadrant) for solutions of elliptical and hyperbolic motion.

In the case of hyperbolic motion the curve of singularities shows that no development in e or $1/e$ converges for all values of M and even the development in powers of $e - e_0$ ($e_0 > 1$) is of no practical use for the circle of convergence (uniformly with M) is limited by the curve and cannot include the region near $e = 1$, the cusp of the curve.

Turning to equation (10) for parabolic motion μ is seen to be a three valued function of $D = 12\sqrt{2kq^{-3/2}t}$. For D real there are two complex roots and one real, the real root increasing monotonically with D . The zeros of the first derivative of $12\mu + \mu^3 + D$ occur at $\mu = \pm 2i$; the Riemann surface of $\mu = \mu(D)$ has branch points at $D = \pm 16i$ and there are no further finite singularities. These singularities limit the radius of convergence and the general usefulness of any development of (the real branch of) μ according to powers of $D - D_0$.

Turning to the nearly parabolic case write equation (9) in the form $F(\epsilon, \mu, D)=0$. Expanding $\sin^{-1} \epsilon^{1/2}\mu$ as a series we obtain

$$0 = -D + 12\mu + \mu^3(1 + \epsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4} \frac{\epsilon\mu^2}{5} + \dots\right), \quad (19)$$

where the right-hand member is an expression of part of the branch of $F(\epsilon, \mu, D)$ for which $\mu=0$ implies $D=0$ (for $|\epsilon\mu^2| < 1$). For this branch of $F(\epsilon, \mu, D)$ the origin is a regular point but it is a pole for every other branch.

Also we have

$$\begin{aligned} \frac{\partial F}{\partial \mu} &= 12 + (1 + \epsilon)\frac{6}{\epsilon}\{(1 - \epsilon\mu^2)^{-1/2} - 1\} \\ &= 12 + \mu^2(1 + \epsilon)6\left(\frac{1}{2} + \frac{1.3}{2.4} \epsilon\mu^2 + \dots\right). \end{aligned} \quad (20)$$

This shows that for D, ϵ and μ real we have

(i) When $0 \leq \epsilon < 1$, the elliptical case, i.e. $1 \geq \epsilon > 0$ F is monotonic increasing with μ for $\epsilon\mu^2 < 1$,

(ii) When $\epsilon \geq 1$, the parabolic (see equation 10) and hyperbolic cases, $0 \geq \epsilon > -1$ F is monotonic increasing with μ and there is a unique real solution of (9) for any real value of D . We also see that for small values of ϵ there are always solutions of $\partial F / \partial \mu = 0$ near the points $\mu^2 = -4$ on the imaginary axis of μ . The existence of these singularities limits the radius of convergence and usefulness of the development of μ as a power series in D with coefficients in ϵ (fixed). The attempt to express the coefficient of μ^3 in (9) as a development in series in order to evaluate the coefficient and transform the equation for solution into an ordinary cubic meets with the same difficulty.

However, let us consider $\mu = \mu(D, \epsilon)$ as a function of ϵ (D real constant) and wish to develop the solution as a Taylor's series proceeding in powers of ϵ with coefficients functions of $\nu = \mu(D, 0)$. It will be necessary to see how the matter is affected by singularities of $\mu = \mu(D, \epsilon)$ for ϵ in the complex domain in the vicinity of the solution $\epsilon=0, \mu=\nu$ on the real axis.

Let us write equation (20) in the form

$$\begin{aligned} \frac{1}{12} \frac{\partial F}{\partial \mu} &= 1 + \frac{1}{2} \left\{ \frac{1 - (1 - \epsilon\mu^2)^{1/2}}{(1 - \epsilon\mu^2)^{1/2}} \right\} + \frac{\mu^2}{4} + \frac{\mu^2}{4} \left\{ \frac{2[1 - (1 - \epsilon\mu^2)^{1/2}]}{\epsilon\mu^2(1 - \epsilon\mu^2)^{1/2}} - 1 \right\} \\ &= 1 + f_1(\epsilon\mu^2) + \frac{\mu^2}{4} + \frac{\mu^2}{4} f_2(\epsilon\mu^2) \end{aligned}$$

Now for the points $\epsilon=0, \mu=\nu, 1 + \mu^2/4 \neq 0$ and $f_1(\epsilon, \mu)=0, f_2(\epsilon, \mu)=0$. Then if m is the lower bound of $|1 + \mu^2/4|$ on the circle $|\mu - \nu| = r$ about $\mu=\nu$ it is necessarily possible to choose r , so that $m > 0$. It is also possible to choose ρ such that $|\epsilon| < \rho$ makes $f_1(\epsilon, \mu) + f_2(\epsilon, \mu) < m$. Hence by Rouché's theorem $\partial F / \partial \mu$ has within the domains $|\mu - \nu| < r, |\epsilon| < \rho$ the same number of zeros as $1 + \mu^2/4$ and since ν is a point on the real axis with no zeros in its vicinity this can be made no zeros. The radius of convergence of the series for μ in ϵ thus shown to exist can be proved at least sufficient for practical needs.

Choose the circle round ν to be

$$\mu = \nu(1 + e^{i\varphi}/5) \quad (21)$$

(e here and for the rest of this paragraph is the exponential). Then the real part of $1 + \mu^2/4$

$$\begin{aligned} &= 1 + \frac{\nu^2}{4} + \frac{\nu^2}{10} \cos \varphi + \frac{\nu^2}{100} \cos 2\varphi \\ &> 1 + \frac{14}{100} \nu^2. \end{aligned}$$

On this circle $f_1(\epsilon\mu^2) + \frac{\mu^2}{4}f_2(\epsilon\mu^2)$

$$= f_1(\epsilon\mu^2) + \frac{\nu^2}{4} \left(1 + \frac{2}{5}e^{i\varphi} + \frac{1}{25}e^{2i\varphi} \right) f_2(\epsilon\mu^2),$$

the modulus of which

$$\leq |f_1(\epsilon\mu^2)| + \frac{\nu^2}{4} \frac{36}{25} |f_2(\epsilon\mu^2)|.$$

Now consider $\epsilon\mu^2$ as the other variable (instead of ϵ). Since the coefficients of $\epsilon\mu^2$ in the series for f_1 and f_2 are positive numbers the maxima of the moduli of the functions for $|\epsilon\mu^2| = \rho$ occur on the positive real axis—that is for $\epsilon\mu^2 = \rho$. Take $\rho = 0.35$, then

$$\left| \begin{array}{l} f_1 < 0.12, \quad |f_2| < 0.38 \\ f_1 + f_2 < 1 + \mu^2/4 \end{array} \right|$$

whence

So that $\partial F/\partial \mu$ has the same number of zeros in the circle (21) with $\epsilon\mu^2$ in the domain $|\epsilon\mu^2| \leq 0.35$ as has $1 + \mu^2/4$ —that is none—and there are no singularities for the values of ϵ and μ satisfying the given conditions. We shall see later that the nearly parabolic solution is not required for $|\epsilon^{1/2}\mu| > 0.58$ —that is $|\epsilon\mu^2| > 0.34$.

The solution of (19) may now be obtained as a Taylor's series of the form

$$\mu = C_0 + C_1\epsilon + C_2\epsilon^2 + \dots \quad (22)$$

either by calculating the necessary differential coefficients or by equating coefficients taking $D = 12\nu + \nu^3$, ν being the solution for $\epsilon = 0$. If this is done we find

$$\begin{aligned} C_0 &= \nu \\ C_1 &= -\frac{\nu^3}{1 + \nu^2/4} \left(\frac{1}{2^2 \cdot 3} + \frac{3}{2^4 \cdot 5} \nu^2 \right) \\ C_2 &= -\frac{\nu^5}{(1 + \nu^2/4)^3} \left(\frac{1}{2^2 \cdot 3 \cdot 5} + \frac{127}{2^5 \cdot 3^2 \cdot 5 \cdot 7} \nu^2 + \frac{1}{2^4 \cdot 5 \cdot 7} \nu^4 - \frac{1}{2^9 \cdot 5^2 \cdot 7} \nu^6 \right) \end{aligned}$$

The disadvantage of this method of solution is that even in the range of appropriateness of the nearly parabolic solution ν may become large and the tabulation for the coefficients correspondingly extended.

The form of the equations determining the coefficients in (22) suggests another solution. The equation determining C_1 is of form

$$C_1(1 + \nu^2/4) = -\nu^3 \text{ (polynomial of degree 2 in } \nu).$$

The polynomial has no term of the first power in ν , so that if we divide throughout by $1 + \nu^2/4$ we can obtain a remainder of the form $\gamma_1\nu^3$ where γ_1 is a numerical constant, so that if we add a term $\gamma_1\nu^3\epsilon$ to the $12\nu + \nu^3$ side of the original equation the coefficient of ϵ would become a polynomial of degree 2 and γ_1 a constant to be determined in the process of equating coefficients. Similarly it is possible to obtain a form of coefficient avoiding fractions for the higher powers of ϵ by equating coefficients in a solution of the form

$$\left. \begin{aligned} D &= 12\sigma + \sigma^3\epsilon^2 \\ &= 12\mu + \mu^3(1 + \epsilon)6 \left(\frac{1}{2 \cdot 3} + \frac{1 \cdot 3}{2 \cdot 4} \frac{\epsilon\mu^2}{5} + \dots \right), \\ \epsilon^2 &= 1 + \gamma_1\epsilon + \gamma_2\epsilon^2 + \dots, \\ \mu &= \sigma(1 + G_1\epsilon + G_2\epsilon^2 + \dots), \end{aligned} \right\} \quad (23)$$

with

$$\begin{aligned} G_1 &= g_{12}\sigma^2, \\ G_2 &= g_{22}\sigma^2 + g_{24}\sigma^4, \\ &\dots \end{aligned}$$

where G_n is a polynomial of degree $2n$ in σ an auxiliary quantity determined by the first equation. Here the first coefficients are

$$\begin{aligned} G_1 &= -\frac{3}{2^2.5}\sigma^2, \\ G_2 &= -\frac{1}{2^2.5^2.7}\sigma^2 + \frac{1}{2^3.5^2.7}\sigma^4, \\ G_3 &= -\frac{13}{3^2.5^3.7}\sigma^2 + \frac{71}{2^3.3^2.5^3.7}\sigma^4 + \frac{1}{2^4.3^2.5^2.7}\sigma^6, \\ G_4 &= -\frac{107}{2^2.3^2.5.7^2.11}\sigma^2 + \frac{6679}{2^4.3^2.5^3.7^2.11}\sigma^4 + \frac{221}{2^6.5^3.7^2.11}\sigma^6 + \frac{43}{2^8.5^3.7^2.11}\sigma^8, \\ G_5 &= -\frac{2^9.103}{3^5.5^7.11.13}\sigma^2 + \frac{214601}{2^4.3^2.5^5.7.11.13}\sigma^4 + \frac{178849}{2^6.3^2.5^5.7^2.11.13}\sigma^6 \\ &\quad + \frac{123791}{2^8.3^2.5^5.7^2.11.13}\sigma^8 + \frac{1213}{2^8.3^2.5^5.7.11.13}\sigma^{10}, \\ c^2 &= 1 - \frac{4}{5}\epsilon - \frac{6}{5^2.7}\epsilon^2 - \frac{52}{3^5.5^3.7}\epsilon^3 - \frac{107}{3^5.7^2.11}\epsilon^4 - \frac{2^{11}.103}{5^5.7^2.11.13}\epsilon^5 \dots, \end{aligned}$$

where the exponent is placed on c so that the first equation can be conveniently written in the same form as that for the parabola and solved by the use of the same table. The extreme value of ϵ for which the nearly parabolic solution is necessary is 0.07 , for which the first neglected term of c^2 is 0.8×10^{-9} .

In the process leading to the previous solution it would have been possible to carry on the division by $(1 + v^2/4)$ a step further to give a remainder of the form $\beta_1 v$ and destroyed the fractional form of the C_1 term in the solution in Taylor's series by adding a term $\beta_1 v \epsilon$ to the left-hand member of the equation determining the coefficients. This suggests a solution of the form

$$12\tau + \tau^3 b = 12\mu + \mu^3(1 + \epsilon)6\left(\frac{1}{2.3} + \frac{1.3}{2.4} \frac{\epsilon \mu^2}{5} + \dots\right),$$

with

$$\begin{aligned} b &= 1 + \beta_1 \epsilon + \beta_2 \epsilon^2 + \dots, \\ \mu &= \tau(1 + H_1 \epsilon + H_2 \epsilon^2 + \dots), \end{aligned}$$

where H_n is a polynomial of degree $2n$ in τ . The first terms of this solution are given by

$$\begin{aligned} H_1 &= \frac{4}{3.5} - \frac{3}{2^2.5} \tau^2, \\ H_2 &= \frac{242}{3^2.5^2.7} - \frac{43}{2^2.5^2.7} \tau^2 + \frac{1}{2^3.5^2.7} \tau^4, \\ &\quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \\ b &= 1 + \frac{4}{3.5} \epsilon + \frac{242}{3^2.5^2.7} \epsilon^2 + \dots \end{aligned}$$

It is a pleasure to acknowledge the helpful conversations I had with Mr. W. B. Smith-White, who kindly read a draft of this section before it was offered as a contribution to him in his capacity of editor.

NUMERICAL CONSIDERATIONS.

Kepler's equation may for purposes of calculation be written in a number of ways according to the tastes of the computer or the tables he has available; among these are

$$\begin{aligned}[M] + \{e\}(\sin E) &= E \\ -\left[\frac{M}{e}\right] + \left\{\frac{1}{e}\right\}(E) &= \sin E \\ [M] + \{e\}(Y) &= \sin^{-1} Y \\ [M] - \{1-e\}(Y) &= \sin^{-1} Y - Y\end{aligned}$$

where $\sin E = Y$. The quantity in the square bracket is put into the product register of the calculating machine, that in the curly bracket in the setting register and the quantity in the plain bracket built up in the multiplier register till the right-hand member of the equation appearing in the product register has the value corresponding to that in the plain bracket. The first two forms, due to Comrie and Strömgren respectively (see Möller, 1933), require a table of sines with argument in decimals of a degree or in radians. The recently published Chambers Six-Figure Mathematical Tables (Comrie, 1949) are most suitable. Reasonably near to perihelion the third and fourth forms are useful. The tables of Möller (1940) and Strömgren (1945) are particularly suitable for the last form, which is valuable in the range of values, to be discussed shortly, when computation with an extra figure is necessary. The last three forms have the advantage that the quantity to appear in the multiplier register, being the argument of the mathematical table, can be more conveniently built up to its full number of tabulated figures. It should be added that the second method can be used even if e is small, since although its reciprocal is large and the significant figures of E/e and M/e are moved relative to those $\sin E$ the same thing occurs with the equation in its original form and indeed (if only E were required) for a five-figure solution of $M = E - e \sin E$ with $e < 0.1$ the value of $\sin E$ would be needed to only four decimals.

If the tables for $\sin E$ extend only to $\pi/2$ the equation may be used past this point in the form

$$\begin{aligned}(\pi - M) - e \sin(\pi - E) &= \pi - E \\ \text{or} \quad \frac{\pi - M}{e} - \frac{\pi - E}{e} &= \sin(\pi - E)\end{aligned}$$

It is well known that the accuracy of solution of Kepler's equation falls off when e tends towards 1. Suppose equation (7) has been solved by using a table of sines. Let the solution obtained be E_1 , $\sin_t E_1$ the value of its sine simultaneously obtained from the table and E the accurate solution.

Then

$$\begin{aligned}M &= E_1 - e \sin_t E_1, \\ \sin_t E_1 &= \sin E_1 + \Delta, \\ E_1 &= E + \delta E,\end{aligned}$$

and

$$\sin_t E_1 = \sin E + \delta \sin E$$

where the last three equations are definitions of Δ , the error of the table and of δE and $\delta \sin E$, the errors in the solutions for E and $\sin E$ respectively. From these equations with (7)

$$\delta E = \frac{e \Delta}{1 - e \cos E} \quad \text{and} \quad \delta \sin E = \frac{\Delta}{1 - e \cos E}$$

If we are working with a table to n figures the maximum error (now called Δ) of the table will be 0.5×10^{-n} and its average value would be half of this.

The rectangular coordinates in the plane of the orbit are

$$\begin{aligned}x_0 &= a (\cos E - e) \\ y_0 &= a(1 - e^2)^{1/2} \sin E\end{aligned}$$

and the maximum errors in these arising from errors in solving Kepler's equation and (another Δ) in extracting $\cos E$ from the tables are

$$\begin{aligned}\delta x_0 &= a \Delta (e \sin E + 1 - e \cos E) / (1 - e \cos E) \\ \delta y_0 &= a(1 - e^2)^{1/2} \Delta / (1 - e \cos E)\end{aligned}$$

The effect that these errors has on the position of a body on the celestial sphere depends on their relation in direction and magnitude to the geocentric distance vector, but as this relation differs for every body and for the same one at different times it is best for the purpose of establishing a measure of the influence of the errors on the position of an object to compare their magnitude with that of the heliocentric distance, r . Now

$$r = a(1 - e \cos E)$$

so that using the relations above

$$\frac{\{(\delta x_0)^2 + (\delta y_0)^2\}^{1/2}}{r} = \frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} \Delta \quad (24)$$

The value of the coefficient of Δ in (24) which may be tolerated is arbitrary, but 3 seems a reasonable figure and one which will not introduce errors from this cause more serious than must be admitted in almost any extended calculation. If the values of M and e are plotted as abscissa and ordinate on a plane, the curve given by (7) and

$$\frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} = 3$$

defines the boundary of the region in which Kepler's equation will give a satisfactory result. Beyond this region is an area in which it is profitable if we want a result accurate to n figures to work with a table to $n+1$ decimals. The boundary of this region is given by

$$\frac{(2 + 2e \sin E)^{1/2}}{(1 - e \cos E)^{3/2}} = 30$$

and beyond this methods adapted for nearly parabolic solutions should be used.

Also consider the equation

$$x_0 = a(\cos E - e)$$

and suppose the possible error in the tabulation of $\cos E$ to be Δ_1 , then

$$\delta x_0 / r = \Delta_1 / (1 - e \cos E) \quad (25)$$

along the extra figure boundary $(1 - e \cos E)^{-1}$ has values from 1.8 to 2.5 and along the nearly parabolic boundary from 7.8 to 8.5, which shows that it is necessary to work with the extra figure, when it is appropriate, even after the determination of E (or $\sin E$). For small geocentric distances, say less than 0.3 astronomical unit, it would be necessary to use the extra figure apart from the considerations arising above.

If we work through the case of the hyperbolic orbit, equation (8), in the same way as has been done for the ellipse we find the boundary beyond which extra figure computation is necessary is given by

$$\frac{(2e \cosh F + 2e \sinh F)^{1/2}}{(e \cosh F - 1)^{3/2}} = 3$$

and that beyond which nearly parabolic solution must be used by

$$\frac{(2e \cosh F + 2e \sinh F)^{1/2}}{(e \cosh F - 1)^{3/2}} = 30$$

Both equations are taken with equation (8) if M is to be plotted against e .

Figure 2 shows these curves which define the regions in which the various types of computation are appropriate. In Figure 3 the area in which nearly parabolic solution is desirable is represented on the plane of e and $\sin E (= \varepsilon^{1/2} \mu)$ M and $\sin E$ are always available when calculating in the ordinary way or with

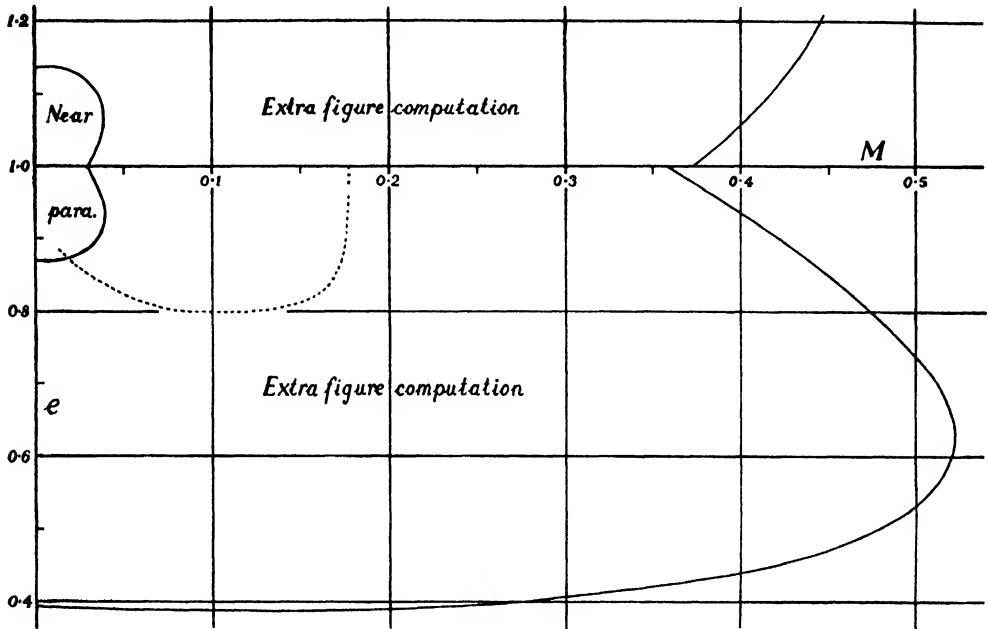


Fig. 2.—Method of solution according to values of e and M .

the extra figure and a quantity approximating to $\varepsilon^{1/2} \mu$ is available at a stage in the nearly parabolic solution which I hope to publish soon so that these diagrams facilitate a decision as to which type of computation is to be used, or in some cases when a change of process is necessary. In doubtful cases either of the possible alternatives should be satisfactory. It may be pointed out that the nearly parabolic solution is not necessary except when $\sin E < 0.53$ or $\sinh F < 0.58$ and by the previous discussion the development in series of the solution for the co-ordinate μ is then permissible.

Many transformations of Kepler's equation have been used to provide solutions, ones of importance being by Tietjen (see Bauschinger, 1934), Howe (see Plummer, 1919) and Oppolzer and Marth (see Marth, 1890b). Oppolzer and Marth, independently, wrote the equation in the form

$$\tan (E - M) = \frac{e \sin M}{\lambda - e \cos M},$$

where

$$\lambda = \frac{E - M}{\sin (E - M)}.$$

Tables for this solution were given by the two authors mentioned and more recently Subbotin (1929) has used it tabulating $\log \lambda$ to seven decimal places

with argument $\tan (E-M)$. It is of interest to examine the range of applicability of this transformation of Kepler's equation as was done for the equation itself in the previous paragraphs.

We obtain

$$\begin{aligned}\delta E &= \frac{\tan (E-M)}{\sec^2 (E-M) \{ \cos (E-M) + (E-M) \sin (E-M) - e \cos M \}} \Delta \\ &= \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M) + (E-M) \sin (E-M) - e \cos M} \Delta\end{aligned}$$

Where Δ is the error of the tabulated value of λ . The ratio of the error arising from δE in the position of the body on the plane of its orbit to the radius vector

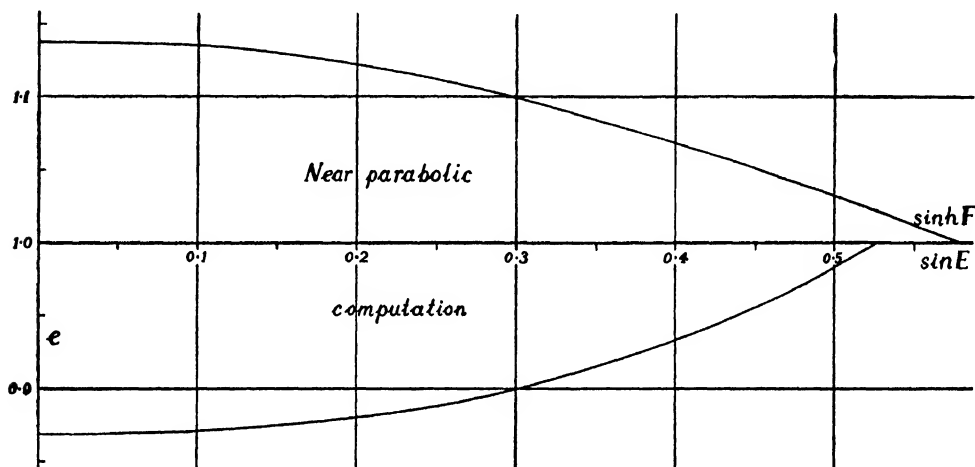


Fig. 3.—Method of solution according to values of e and $\sin E$ (or $\sinh F$).

is

$$\begin{aligned}\frac{\{(\delta x_0)^2 + (\delta y_0)^2\}^{1/2}}{r} &= \left\{ \frac{1+e \cos E}{1-e \cos E} \right\}^{1/2} \delta E \\ &= \left(\frac{1+e \cos E}{1-e \cos E} \right)^{1/2} \frac{\frac{1}{2} \sin 2 (E-M)}{\cos (E-M) + (E-M) \sin (E-M) - e \cos M} \Delta\end{aligned}\quad (26)$$

If we are prepared to allow the coefficient of Δ in this equation to attain the value 3 and as before map the boundary of the area for which the transformation is applicable, we are applying a rather less severe test since the error in the equation includes the effect arising only from the error in calculating E and neglects errors in the tables subsequently used for computing x_0 and y_0 . Nevertheless, the boundary which is shown by the dotted curve on Figure 2 indicates that while the method of solution does represent an improvement on that using a table of sines to the same number of figures, it does not improve on the accuracy obtained by using the sine table to an extra figure nor encroach appreciably on the area in which a nearly parabolic solution is needed.

It is thus not possible to dispense with extra figure calculation unless we are willing to extend unduly the tabulation for nearly parabolic solutions. Equations (25) and (26) show that however accurately E may be determined the solution in terms of eccentric anomaly leads to difficulties when e is nearly 1 and E is small.

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The following bibliography is supplementary to the references given by Radau (1900), Bauschinger (1901 and 1934), Herglotz (1906) and Wintner (1941). Material listed by these authors has not been repeated unless referred to in my article. The titles of the references do not always show satisfactorily the aspect of Kepler's Problem with which they deal, so they are omitted and the contents indicated by a code, which has the further advantage of economy.

- G, indicates a general account such as might be given by a text book, a review article or an article chiefly didactic in purpose,
- T, that the main interest is theoretical,
- S, an article whose main purpose is to describe or discuss a method of obtaining a solution of Kepler's Problem, and
- I, a solution depending on numerical integration or the application of finite differences.
- e, indicates that the article refers to elliptic motion,
- n, to nearly parabolic motion, and
- p, to parabolic motion.
- s, indicates a solution in power series,
- f, a solution in trigonometric series,
- g, that the solution is graphical or mechanical and
- c, that a numerical solution is given (c is only used if two methods are described otherwise solutions may be assumed to involve numerical methods),
- t, indicates that tables are given to aid the purpose of the article and
- z, that I have not seen the article myself and depend on a review or abstract for its description.

This bibliography is meant to be fairly comprehensive for categories S and T. Developments whose main application lies in the study of perturbed motion have usually been omitted except for some borderline cases under the heading I. The historical aspect has been neglected entirely but those who are interested will find valuable guidance in Radau (1900), Herglotz (1906) and Wintner (1941); and the bibliography of Houzeau and Lancaster (1887, 1889) gives many references, nearly all of which were inaccessible to me. The collected works of Kepler have been edited by Frisch (1858-71) and a recent account of "de motibus stellæ Martis" is given by Pannekoek (1948).

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A NEW METHOD OF MEASUREMENT OF THE SURFACE TENSION OF VISCOUS LIQUIDS.

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INTRODUCTION.

The measurement of the surface tension of viscous liquids, such as molasses, by usual methods, is often hindered by factors arising from the high viscosity of the liquid. Thus L'eaute (1935) in measuring the surface tension of tars and bitumen by capillary rise, notes that equilibrium condition for bitumen is reached in 360 hours. In the Sugden bubble pressure method, the time required to blow the bubble with no viscosity interference is of the order of ten minutes, an unpracticably long time. With the Du Nouy tensiometer, the break point for molasses is poorly defined.

The method now presented is a development of the Eötvös reflection method for sessile drops and is independent of viscosity. It may be applied to the measurement of the surface tension of liquids in general, with particular value for viscous liquids such as molasses and other concentrated sugar syrups.

Previous methods of measuring surface tension from the shape of sessile drops have relied on actual measurement of radii of curvature and other drop dimensions, usually made on the profile of the drop. Thus Worthington (1881) projected the form of *hanging* drops of water on a screen and measured radii of curvature and the volume of the drop. His work was amplified by Ferguson (1912), who photographed the drop. Moser (1927) calculated surface tensions from observations made vertically on sessile drops, and proposed refinements of the original method used by Eötvös (1886). Moser's observations were made with a telescope, to measure the vertical distance between two points of reflection on the curved surface of the drop and also the angles at which the light was reflected. Kemball (1946) employed side view illumination and a comparator for measuring sessile drops of mercury, and calculated the surface tension from the height and equatorial diameter of the drop. Taylor and Alexander (1944) also used side view illumination. They photographed sessile drops formed on the end of a brass tube and, from the photograph, measured the height of the drop above its equatorial plane, the equatorial diameter and thence calculated the surface tension.

EXPERIMENTAL.

In the method now presented, a drop of liquid on a plane surface (not wetted by the liquid) is illumined from above by two point sources of light, and photographed by a camera placed between the lights. A millimetre scale is also included in the photograph, which shows the images of the lights reflected by the drop. The distance between these images is measured by reference to the photographed millimetre scale. The equatorial diameter of the drop is also measured from the photograph. The distance from the light to the drop, and the distance between the lights are also measured. Figure 1, which is not

drawn to scale, illustrates the method of deriving the radius of curvature of the drop from these measurements.

From a consideration of the similar triangles L_1L_2F and I_1I_2F , we get

$$\frac{a}{x} = \frac{y}{\text{focal length}}$$

$$= \frac{y}{\frac{1}{2}b}$$

$$\text{Then } b = \frac{2xy}{a} \dots\dots\dots (1)$$

where b = the radius of curvature at the vertex of the drop.

x = the distance of the drop from the light.

y = the distance between the images on the drop.

a = the distance between the lights.

x and a are large in comparison with b and y . In the actual apparatus x was 68 cm., a was 47 cm., while b and y were usually of the order of 0.3 cm.

The value of b thus found, together with r , the equatorial radius of the drop (measured from the photograph) is then used to calculate the surface tension by means of a formula,

$$\text{Surface tension} = \gamma = \frac{r^3}{b-r} \times \frac{dg}{6} \text{ dynes cm.}^{-1}.$$

where d = density difference between liquid and surrounding gas, in gm. cm.⁻³.
 g = gravitational acceleration in cm. sec.⁻².

DEDUCTION OF THE FORMULA.

The formula above was obtained from a study of the tables of Bashforth and Adams (1883). These tables give the values of b/x at a series of values of a dimensionless quantity, defined as

$$\beta = \frac{gdb^2}{\gamma}$$

where b is the radius of curvature at the vertex of the drop and γ is the surface tension.

x is the horizontal distance from the surface of the drop to its axis. The maximum value of x we have designated as r and thus obtained values of b/r as an empirical function of β . Empirically it has been found that there is an

almost linear relationship between β and $\frac{b^2}{r^2} \left(\frac{b}{r} - 1 \right)$ and the ratio $\frac{\beta}{\frac{b^2}{r^2} \left(\frac{b}{r} - 1 \right)}$

has an almost constant value of 6.0 over the range $0 < \beta < 4$. This ratio $\frac{\beta}{\frac{b^2}{r^2} \left(\frac{b}{r} - 1 \right)}$

cancels to $\frac{r^3}{b-r} \frac{dg}{\gamma}$ which we will designate as α . Values of β , $\frac{b^2}{r^2} \left(\frac{b}{r} - 1 \right)$ and

this quotient α are given in Table I.

TABLE I.
Values of the Dimensionless Quantities Concerned with the Shape of Drops Calculated from the Tables of Bashforth and Adams.

| $\beta = \frac{gdb^3}{\gamma}$ | $\frac{b^3}{r^3} \left(\frac{b}{r} - 1 \right)$ | $\alpha = \left(\frac{r_3}{b-r} \frac{dg}{\gamma} \right)$ |
|--------------------------------|--|---|
| 0.1 | 0.01656 | 6.037 |
| 0.2 | 0.03316 | 6.031 |
| 0.3 | 0.049735 | 6.032 |
| 0.4 | 0.06626 | 6.036 |
| 0.5 | 0.08275 | 6.042 |
| 0.6 | 0.099245 | 6.045 |
| 0.7 | 0.115755 | 6.047 |
| 0.8 | 0.13226 | 6.049 |
| 0.9 | 0.14879 | 6.049 |
| 1.0 | 0.16533 | 6.049 |
| 1.2 | 0.19845 | 6.047 |
| 1.4 | 0.231675 | 6.043 |
| 1.6 | 0.26497 | 6.038 |
| 1.8 | 0.29836 | 6.033 |
| 2.0 | 0.331845 | 6.027 |
| 2.2 | 0.36543 | 6.020 |
| 2.4 | 0.29910 | 6.013 |
| 2.6 | 0.43290 | 6.006 |
| 2.8 | 0.46675 | 5.999 |
| 3.0 | 0.50073 | 5.991 |
| 4.0 | 0.67207 | 5.952 |
| 5.0 | 0.84569 | 5.912 |
| 6.0 | 1.0214 | 5.874 |
| 7.0 | 1.1991 | 5.837 |
| 8.0 | 1.3787 | 5.802 |
| 9.0 | 1.56015 | 5.768 |
| 10.0 | 1.7431 | 5.737 |
| 15.0 | 2.68035 | 5.596 |
| 20.0 | 3.6494 | 5.480 |

It will be seen that for the range $\beta=0.1$ to $\beta=4.0$ the proportionality factor is 6.00 ± 1 per cent. maximum variation.

Thus

$$\frac{r^3}{b-r} \frac{dg}{\gamma} = 6.0$$

or
$$\gamma = \frac{r^3}{b-r} \frac{dg}{6.0} \dots\dots\dots (2)$$

where γ =the surface tension in dynes cm.⁻¹.

r =the equatorial radius of the drop in cm.

b =the radius of curvature at the vertex of the drop in cm.

g =the gravitational acceleration in cm. sec.⁻¹.

d =density difference between liquid and surrounding gas in gm. cm.⁻³.

This equation used in conjunction with (1) provides an easy method of determining the surface tension from the measurement of the images reflected in sessile droplets.

Maximum Size of Drops.

In using the equation

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6.0}$$

It is necessary for the drops to conform to the requirement that β be not greater than 4.0. This is evident from Table I, and therefore places an upper limit on the size of the drop. This maximum size can be deduced in the following manner :

The upper limit of the size of the drop depends on the surface tension and the density of the liquid under investigation.

Taking as the limiting condition

$$\beta = 4.0$$

$$\text{i.e.} \quad g \frac{db^2}{\gamma} = 4.0$$

this gives the limiting value of b as

$$b = \sqrt{\frac{4\gamma}{gd}}$$

Substituting this value of b in equation (2), we get

$$2 \sqrt{\frac{r^3}{\gamma} - r} \frac{gd}{\gamma} = 6.0$$

$$\text{whence} \quad gdr^3 + 68r - 12 \sqrt{\frac{\gamma^3}{gd}} = 0 \dots\dots\dots (3)$$

This is an expression for the limiting radius (r) of the droplet.

On substituting the approximate values for the density and surface tension of the liquid concerned, this equation may be solved numerically to give the maximum value of r .

Thus, for one of the more viscous liquids which it is proposed should be examined by this method, namely molasses, we have approximately

$$d = 1.4 \text{ gm. cm.}^{-3}$$

$$\gamma = 65 \text{ dynes cm.}^{-1}.$$

Substituting these values in equation (3), we get

$$1372r^3 + 390r - 169.6 = 0$$

or

$$r = 0.320 \text{ cm.}$$

This means that the approximation implicit in equation (2) may be used with molasses for all drops up to a limiting diameter of 6.4 mm. This is quite a reasonably large drop.

For ethyl alcohol, a liquid with a low specific cohesion, we have

$$d = 0.8 \text{ gm. cm.}^{-3}$$

$$\gamma = 22 \text{ dynes cm.}^{-1}.$$

Substituting these values in (3) and solving for r as above, we obtain

$$r = 0.246 \text{ cm.}$$

Thus the maximum diameter of a drop of ethyl alcohol to be tested by this method is 0.49 cm.

Taking mercury as an example of a liquid with high surface tension, we have

$$d = 13.6 \text{ gm. cm.}^{-3}$$

$$\gamma = 488 \text{ dynes cm.}^{-1}$$

from which the maximum value of r is $r = 0.281 \text{ cm.}$, whence the maximum diameter is 0.56 cm.

In all cases examined it seems that the proposed method can be used over a reasonable range of drop diameter.

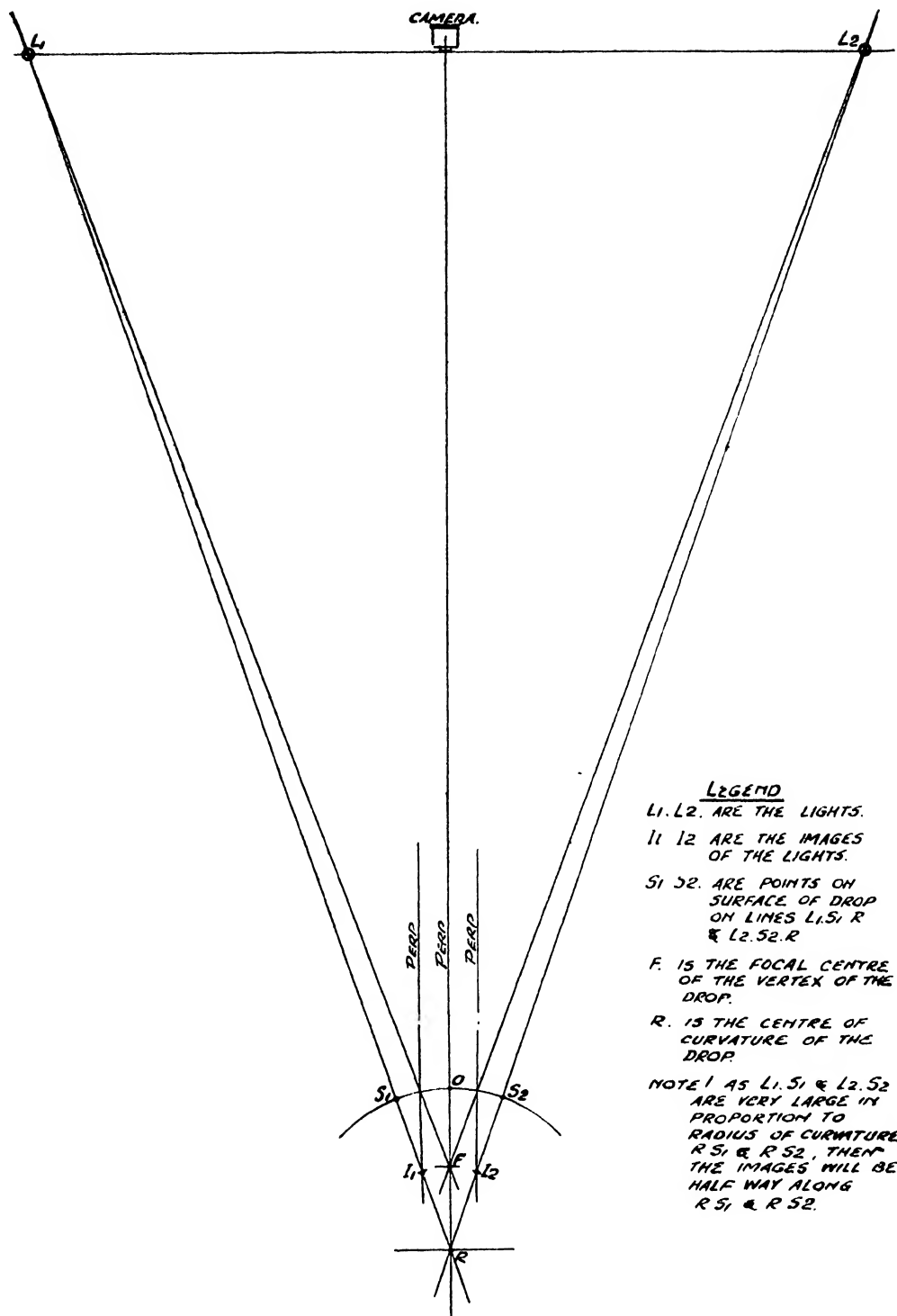


Fig. 1.

DISCUSSION.

The method proposed for the measurement of surface tension involves the measurement on a sessile drop, of the equatorial radius (r) and the radius of curvature at the vertex (b). It has been shown that these two quantities are related to the surface tension (γ), and the density of the liquid by the simple approximate formula

$$\gamma = \frac{r^3}{b-r} \frac{dg}{6}$$

This equation holds with an accuracy of 1 per cent. for all droplets below a certain limiting size. This limiting size depends on specific cohesion of the liquid concerned.

The method is particularly valuable for viscous liquids, since, being essentially a static method, it avoids errors arising from the slow attainment of equilibrium in such more familiar methods as the drop weight, ring, capillary rise and bubble pressure methods.

The experimental method is outlined in this paper and consists essentially of photographing a droplet of the liquid, illumined by two point sources of light. The results obtained from the examination of a number of standard liquids, by this method, will be presented in a later paper.

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THE CHEMISTRY OF RUTHENIUM.

PART VI. THE EXISTENCE OF THE TRIS-O-PHENANTHROLINE RUTHENIUM II AND TRIS-O-PHENANTHROLINE RUTHENIUM III IONS IN ENANTIOMORPHOUS FORMS.

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Manuscript received, September 8, 1949. Read, October 5, 1949.

The resolution of tris 2:2' dipyridylruthenium II bromide into optical forms of great stability was achieved by Burstall (1936), through the tartrate, thus demonstrating the octahedral distribution of the groups about hexavalent bivalent ruthenium. Recently, the analogous tris o-phenanthroline compounds, $\text{Ru}(\text{phenan})_3\text{X}_2$, were isolated (Dwyer, Humpoletz and Nyholm, 1946), but although the complexes were of great stability, and obviously of similar composition to the dipyridyl compounds, attempts at resolution through the tartrate, acid tartrate, bromcamphorsulphonate, and camphorsulphonate failed. In this paper the resolution of the tris o-phenanthroline complexes, through the antimonyl tartrate, is described.

When a solution of potassium antimonyl tartrate was added to a solution of tris o-phenanthroline ruthenium II chloride an orange crystalline precipitate resulted. This was found to be the almost pure d, tris-o-phenanthroline ruthenium II antimonyl tartrate, whilst the residual solution was strongly laevo rotatory. The conditions of precipitation were not critical, since the antimonyl tartrate of the d form appeared to be very insoluble, whilst the antimonyl tartrate of the l form was very soluble. Addition of a very large excess of potassium antimonyl tartrate failed to precipitate the laevo form. The crystalline d form was too insoluble in water to be crystallised easily, but was purified by solution in dilute alkali, followed by reprecipitation with acetic acid. The optically active acid radicle was eliminated from the purified material by solution in alkali and precipitation of either the perchlorate or iodide by the addition of sodium perchlorate or potassium iodide. These salts could be crystallised from water, but the perchlorate was the more suitable from the point of view of solubility. The perchlorate of the laevo form was obtained from the original laevo chloride solution by the addition of sodium perchlorate, and crystallised several times from warm water.

The optical forms were notably stable and could be crystallised repeatedly from hot water or alcohol, dissolved in six normal sulphuric acid or kept in aqueous solution at room temperature for over two months without change of rotation. The specific rotations of the forms were as follows: $[\alpha]_{\text{D}}^{20} = +1340^\circ$ and -1328° ; and $[\alpha]_{5461}^{20} = +2559^\circ$ and -2550° . It is thus evident that the substance has a very large abnormal rotatory dispersion, and probably, when the complete rotatory dispersion curve is obtained, an anomalous rotatory dispersion. Burstall found $[\alpha]_{5791}^{25} = +860^\circ$ and -815° for the dipyridyl compound. It is probable that this substance too possesses an abnormal rotatory dispersion.

The optical forms were oxidisable with ceric nitrate to the blue ruthenium III complex, which was unstable except in high concentrations of acid (Dwyer, Humpoletz and Nyholm, 1946). The potential of the reaction Ru(phenan)^{++} d or l form $\rightarrow \text{Ru(phenan)}^{+++}$ in six normal sulphuric acid at 0°C . was found to be $1.17 \text{ volts} \pm 0.003 \text{ volt}$. The same value was obtained from the racemate by determining the potential with a mixture of the two optical forms. (See also Dwyer, 1949.) This is the first occasion that the redox potential of an enantiomorphous form has been compared with the racemate. It is unfortunate that the instability of the system precluded a more accurate value of the potentials.

When d or l tris-o-phenanthroline ruthenium II perchlorate in six normal sulphuric acid was oxidised with ceric nitrate the resulting blue solution containing the tris-o-phenanthroline ruthenium III ion was found to be optically active, but the rotation was different. The activity was lost rapidly at 20°C ., but if the solution was immediately reduced with ferrous sulphate, the active ruthenium II compound was regenerated with its rotation unchanged. Since the ruthenium III complex could not be isolated the specific rotation has been calculated for the ion $\text{Ru(phenan)}_3^{+++}$. For comparison the rotation of the ion Ru(phenan)_3^{++} are also calculated.*

| Ion. | NaD. | Hg ₅₄₆₁ . |
|-------------------------------------|--------|----------------------|
| d Ru(phenan)_3^{++} | +1834° | +3494° |
| l Ru(phenan)_3^{++} | -1818° | -3482° |
| d $\text{Ru(phenan)}_3^{+++}$ | +584° | +2330° |
| l $\text{Ru(phenan)}_3^{+++}$ | -568° | -2354° |

It is evident that the ion $\text{Ru(phenan)}_3^{+++}$ also has an abnormal rotatory dispersion. The resolution of hexacovalent ruthenium III complexes has already been carried out by Werner and Smirnoff (1920) and Charonnat (1931). The present observations are of particular interest, however, in that they provide a unique demonstration of the similarity of the oxidised and reduced forms of the o-phenanthroline complex, as well as of the essential simplicity of the oxidation/reduction reaction.

Preliminary experiments with the d form of the dipyriddy complex ion Ru(dipy)_3^{++} show that this is also oxidisable with persistence of the optical activity, but the sign of the rotation is changed on oxidation. The results of the experiments on this compound, the resolution of the nickel and ferrous tris-o-phenanthroline complexes, and the complete rotatory dispersion curves for a number of such complexes will be published in subsequent communications.

EXPERIMENTAL.

(A 2 dm. tube was used for all determinations of the rotation.)

d-Tris-(o-Phenanthroline)-Ruthenium II d-Antimonyl Tartrate Dihydrate.

Tris-o-phenanthroline ruthenium II iodide (Dwyer, Humpoletz and Nyholm, 1946), 1.3 g., was dissolved in 100 mls. of hot water, and excess of silver chloride added. The mixture was shaken for five to ten minutes to transform the iodide to the chloride, and filtered with the addition

* In making the transformation from the specific rotations of the salts to the specific rotations of the ions in the preliminary note to *Nature*, 163, 918 (1949) an error was made in the calculations.

of filter paper pulp. Potassium antimonyl tartrate (0.5 g.) in 30 mls. of water was added slowly to the cold chloride, with scratching. The voluminous orange-yellow precipitate was washed several times with water and dissolved with shaking in 75 mls. of cold N/20 sodium hydroxide. Dilute acetic acid was then added until acid, and a small volume of potassium antimonyl tartrate solution, when the substance reprecipitated as orange prismatic needles. It was insoluble in alcohol and sparingly soluble in water, but dissolved easily in the presence of a trace of alkali.

A 0.02% solution in M/100 NaOH gave $\alpha = +0.30^\circ$, whence $[\alpha]_D^{20} = +750^\circ$.

Found: N = 6.84%; Sb = 19.45%.

Calculated for $[\text{Ru}(\text{Cl}_{12}\text{H}_8\text{N}_2)_2][\text{SbO}_4\text{C}_4\text{H}_4\text{O}_6]2\text{H}_2\text{O}$: N = 6.82%; Sb = 19.48%.

d-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.

The d-antimonyl tartrate (0.6 g.) was dissolved in N/20 caustic soda (50 mls.) and the solution filtered. Sodium perchlorate solution (3 N approx.) was added slowly in excess, and the resulting orange-yellow precipitate filtered and washed with ice water containing a little perchloric acid. It was finally crystallised twice from warm water containing a trace of perchloric acid. Alternatively it could be crystallised from warm methanol by the addition of ether. The substance gave micro prismatic needles, which were easily soluble in warm water and alcohol. It was much more soluble than the perchlorate of the racemate.

A 0.205% solution in water gave $\alpha_D = +0.55^\circ$ and $\alpha_{5461} = +1.05^\circ$; whence $[\alpha]_D^{20} = +1340^\circ$ and $[\alpha]_{5461}^{20} = +2560^\circ$.

Found: Ru = 11.7%; N = 9.87%.

Calculated for $[\text{Ru}(\text{C}_{12}\text{H}_8\text{N}_2)_3][(\text{ClO}_4)_2\text{H}_2\text{O}]$: Ru = 11.8%; N = 9.78%.

l-Tris-(o-Phenanthroline) Ruthenium II Perchlorate Monohydrate.

The original solution left after addition of potassium antimonyl tartrate contained approximately half of the substance taken, and was strongly laevo. It was treated with a further portion of antimonyl tartrate solution containing 0.4 g. and cooled in ice to remove traces of the d form. After filtration, the solution was treated with sodium perchlorate solution, and the resulting orange-yellow precipitate of the active perchlorate crystallised twice from warm water containing a trace of perchloric acid. The substance crystallised in orange-yellow micro prismatic needles.

A 0.0211% solution in water gave $\alpha_D = -0.56^\circ$ and $\alpha_{5461} = -1.08^\circ$; whence $[\alpha]_D^{20} = -1328^\circ$ and $[\alpha]_{5461}^{20} = -2557^\circ$.

Found: Ru = 11.9%; N = 9.65%.

Calculated for $[\text{Ru}(\text{C}_{12}\text{H}_8\text{N}_2)_3][(\text{ClO}_4)_2\text{H}_2\text{O}]$: Ru = 11.8%; N = 9.78%.

The Redox Potentials of the d and l Forms and the Racemate.

Approximately M/800 solutions of the two optical forms as the perchlorates dissolved in sulphuric acid 6 N were placed in a redox assembly (Dwyer, 1949) and cooled to 0°C . Half of the theoretical amount of ceric nitrate solution necessary for the oxidation to the ruthenium III complex was added, and the maximum potential determined. For the potential of the racemate equal volumes of the d and l forms were mixed and treated as before with ceric nitrate.

d form : $E = 0.936\text{ v.}$; $E_h = 1.169\text{ v.}$

l form : $E = 0.933\text{ v.}$; $E_h = 1.166\text{ v.}$

Racemate : $E = 0.934\text{ v.}$; $E_h = 1.167\text{ v.}$

Previous work on this system (Dwyer, Humphreys and Nyholm, 1946; Dwyer, 1949) has shown that the potential is not reproducible to more than about 5 mv., so that it can be assumed that the potentials of the optical forms and the racemate are the same within the limits imposed by the instability of the system.

The Persistence of Optical Activity of the Complex Cation after Oxidation.

The d and l perchlorates in sulphuric acid 6 N were treated with drops of ceric nitrate (approx. 0.1 N in 1 N nitric acid) until the colour changed to blue. The amounts of oxidising agent needed were so small that the concentration change was neglected. The oxidised solution was immediately tested for optical activity, which was found to be still present, but the angle of rotation was smaller. A crystal of ferrous sulphate then added to each regenerated the complex ruthenium II cation, and the rotation rose to the original value.

A 0.0082% solution of the d perchlorate after oxidation gave $\alpha_D = +0.07^\circ$ and $\alpha_{5461} = +0.28^\circ$; whence the specific rotation of the d form of the ion $\text{Ru}(\text{phenan})_3^{+++}$ $[\alpha]_D^{20} = +584^\circ$ and $[\alpha]_{5461}^{20} = +2330^\circ$.

A 0.0084% solution of the l perchlorate after oxidation gave $\alpha_D = -0.07^\circ$ and $\alpha_{5461} = -0.29^\circ$; whence the specific rotation of the l form of the ion $\text{Ru}(\text{phenan})_3^{+++}$ $[\alpha]_D^{20} = -568^\circ$ and $[\alpha]_{5461}^{20} = -2354^\circ$.

SUMMARY.

The resolution of tris-o-phenanthroline ruthenium perchlorate has been carried out through the antimonyl tartrate. The enantiomorphous forms were notably stable, and showed a very large abnormal rotatory dispersion. They were oxidisable to the blue tris-o-phenanthroline ruthenium III cation, which was also optically active. Within the limits imposed by the instability of the system, the redox potentials of the enantiomorphous forms and the racemate were the same.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss Fildes for the analyses, and to the Research Fund of the University of Sydney for an assistantship that has enabled one of us (E.C.G.) to take part in this investigation.

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THE CHEMISTRY OF RUTHENIUM.

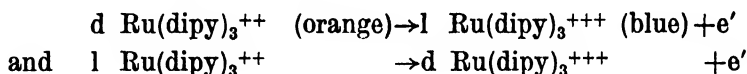
PART VII. THE OXIDATION OF D AND L TRIS 2 : 2' DIPYRIDYL RUTHENIUM II IODIDE.

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and (MISS) E. C. GYARFAS, M.Sc.

Manuscript received, September 8, 1949. Read, October 5, 1949.

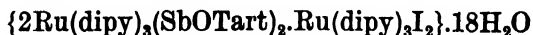
In previous papers (Dwyer and Gyarfás, 1949) it was shown that when d and l tris-o-phenanthroline ruthenium II perchlorates were oxidised with ceric nitrate, the resulting blue solutions of the tris-o-phenanthroline ruthenium III ion were still optically active, but the angles of rotation for the mercury line 5461 and the sodium D line were considerably smaller. It was inferred from these observations that the rotations of the complex ions in the oxidised and reduced forms were not necessarily different but that both ions possessed very large abnormal rotatory dispersions.

The oxidation of the d and l forms of the analogous tris-2 : 2'-dipyridyl ruthenium II ion has now been studied, and it is found that the rotation persists as before but the sign is changed.



After reduction the original ruthenium complex is regenerated, unaltered in the sign or magnitude of the rotation. This unique effect is due to anomalous rotatory dispersion, for the orange ruthenium II complex ion shows no absorption maximum in the visible, whilst that of the blue ruthenium II complex ion is at 5600 Å. The complete absorption and rotatory dispersion curves of this and the analogous iron, osmium and nickel compounds will be described in subsequent communications.

Burstall (1936) resolved tris-2 : 2'-dipyridyl ruthenium II bromide hexahydrate, $\text{Ru(dipy)}_3\text{Br}_2 \cdot 6\text{H}_2\text{O}$ and found $[\alpha]_{5791}^{25} = +860^\circ$ and -815° . The separation was achieved by the use of ammonium d and l tartrates, since the pure laevo form could not be obtained from the mother liquors from which the less soluble d-tris-dipyridyl ruthenium II d tartrate had been crystallised. Since ammonium l tartrate was unavailable it was necessary to devise another procedure for the isolation of the pure laevo form. This was carried out either by fractional crystallisation of the antimonyl tartrate, when the laevo form crystallised first and the dextro form was subsequently isolated as the d tartrate; or more expeditiously as the lattice compound laevo



This curious substance which could be recrystallised either from potassium iodide or potassium antimonyl tartrate solution, crystallised out first when potassium iodide was added to the mixed antimonyl tartrates. It can also be prepared directly by adding potassium antimonyl tartrate to the racemic iodide.

EXPERIMENTAL.

The Resolution of Tris-2 : 2-Dipyridyl Ruthenium II Iodide.

The racemic iodide $\text{Ru}(\text{dipy})_3\text{I}_3 \cdot 3\text{H}_2\text{O}$ was prepared as described previously (Dwyer, 1949). The iodide (2 g.) in hot water (150 mls.) was transformed to the antimonyl tartrate by shaking with silver antimonyl tartrate (0.9 g.) and filtering from silver iodide and the slight excess of silver antimonyl tartrate. The bright orange-red solution was evaporated to 60 mls. and cooled when 1 $\text{Ru}(\text{dipy})_3(\text{SbO} \cdot \text{Tart})_2$ crystallised out. The red crystals were freed from adherent liquid between filter papers, dissolved in N/100 sodium hydroxide (100 mls.) (to destroy the antimonyl tartrate radicle) and precipitated as the iodide by fractional addition of potassium iodide solution. The laevo form was found in the least soluble fractions and purified by recrystallisation from hot water. The mother liquors from the initial antimonyl tartrate solution were precipitated with potassium iodide, and the resulting iodide transformed to the chloride by shaking with silver chloride. The solution of the chloride was then treated with ammonium d tartrate and the dextro form isolated as described by Burstall (*loc. cit.*).

The alternative method, which was found to be more efficient, consisted in taking the antimonyl tartrate solution (100 mls.) prepared from the racemic iodide (2 g.) and fractionally precipitating with dilute potassium iodide solution. The least soluble fractions of red plates and prisms of the lattice compound (*vide supra*) were replaced sharply by much lighter orange-red micaceous plates of the dextro iodide as the fractionation proceeded. An even sharper separation could be achieved by making the solution alkaline with caustic soda as soon as the plates of the dextro form appeared. In this way the antimonyl tartrate radicle was destroyed and only the least soluble dextro iodide precipitated.

The lattice compound was recrystallised either from water, potassium iodide solution or potassium antimonyl tartrate solution—the same substance always being obtained. The crystals became scarlet red in a desiccator or on warming, but regained their lighter colour on standing in moist air. The pure laevo iodide was obtained by solution in sodium hydroxide solution, followed by addition of potassium iodide.

The d and l iodides were crystallised several times from hot water and obtained finally in orange-red micaceous plates.

A 0.0408% solution of the lattice compound in water gave $\alpha_D^{20} = -0.47^\circ$ (2 dm. tube), whence $[\alpha]_D^{20} = -576^\circ$.

A 0.040% solution of the laevo iodide in water in a 2 dm. tube gave $\alpha_D^{20} = -0.65^\circ$ and $\alpha_{5461}^{20} = -0.62^\circ$, whence $[\alpha]_D^{20} = -819^\circ$ and $[\alpha]_{5461}^{20} = -775^\circ$.

A 0.040% solution of the dextro iodide in water gave $\alpha_D^{20} = +0.65^\circ$ and $\alpha_{5461}^{20} = +0.62^\circ$, $[\alpha] = +820^\circ$ and $[\alpha]_{5461}^{20} = +775^\circ$.

Analytical Data.

Found : I = 7.4% ; Sb = 14.05% ; N = 7.34%.

Calculated for $2\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{SbO} \cdot \text{C}_4\text{H}_4\text{O}_6)_2 \cdot \text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{I}_3 \cdot 18\text{H}_2\text{O}$: I = 7.35% ; Sb = 14.18% ; N = 7.34%.

Found, for d form : Ru = 11.60%. Calculated for $\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{I}_3 \cdot 3\text{H}_2\text{O}$: Ru = 11.56%.

The Oxidation of d and l Tris-Dipyridyl Ruthenium III Iodides.

Solutions of the d and l iodides (0.02%) in 1 N sulphuric acid were oxidised with solid ceric ammonium nitrate. The orange solutions first became brown due to the liberation of iodine, which was then further oxidised to iodate and then blue coloured due to the $\text{Ru}(\text{dipy})_3^{+++}$ ion. The oxidised solutions were immediately examined for rotation.

l form (oxidised) $\alpha_D^{20} = +0.11^\circ$ (2 dm. tube), $\alpha_{5461}^{20} = +0.08^\circ$ (2 dm. tube)

d form (oxidised) $\alpha_D^{20} = -0.12^\circ$ (2 dm. tube), $\alpha_{5461}^{20} = -0.07^\circ$ (2 dm. tube).

The specific rotations of the oxidised solutions for the ion $\text{Ru}(\text{dipy})_3^{+++}$ compared with the ion $\text{Ru}(\text{dipy})_3^{++}$ are shown in the table below.

| Ion. | $[\alpha]_D^{20}$ | $[\alpha]_{5461}^{20}$ | $[\alpha]_{5791}^{25}^*$ |
|---|-------------------|------------------------|--------------------------|
| d $\text{Ru}(\text{dipy})_3^{+++}$ (by oxidation of l $\text{Ru}(\text{dipy})_3^{++}$) | +426° | +310° | — |
| l $\text{Ru}(\text{dipy})_3^{+++}$ (by oxidation of d $\text{Ru}(\text{dipy})_3^{++}$) | —465° | —271° | — |
| d $\text{Ru}(\text{dipy})_3^{++}$ | +1269° | +1200° | +1264° |
| l $\text{Ru}(\text{dipy})_3^{++}$ | —1270° | —1200° | —1198° |

* Calculated from Burstall (*loc. cit.*).

After the rotations were determined the solutions were reduced by the careful addition of ferrous sulphate crystals, and the original ruthenium II complex was regenerated with its rotation unchanged in each instance. During the time of the measurement, therefore, racemisation had not occurred.

SUMMARY.

Tris-dipyridyl ruthenium II iodide has been resolved through the curious lattice compound $\{2\text{Ru}(\text{dipy})_3(\text{SbO.Tart})_2.\text{Ru}(\text{dipy})_3\text{I}_2\}18\text{H}_2\text{O}$. The d and l forms when oxidised with ceric nitrate underwent inversion of the sign of the rotation for both the Na_D and Hg_{5461} lines due to the change in the absorption spectrum in passing from the ion $\text{Ru}(\text{dipy})_3^{++}$ to $\text{Ru}(\text{dipy})_3^{+++}$, and the original rotation was regained in sign and magnitude on reduction.

ACKNOWLEDGEMENTS.

The authors are indebted to Dr. F. Lions for the preparation of dipyridyl, to Miss J. Fildes for microanalyses, and one of us (E.C.G.) is indebted to the Research Committee of the University of Sydney for a research assistantship.

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 Dwyer and Gyarfás, 1949. *Nature*, 163, 918.
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COMPLEX COMPOUNDS OF AUROUS HALIDES AND AUROUS CYANIDE WITH DIPHENYLMETHYL AND DIMETHYLPHENYL ARSINE.

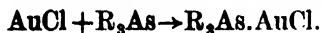
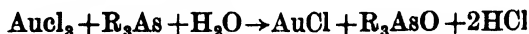
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Manuscript received, September 8, 1949. Read, October 5, 1949.

The tertiary aliphatic arsine and phosphine complexes of cuprous, argentous and aurous halides have been described by Mann and Purdie (1936), who found that one molecule of arsine or phosphine was coordinated with the metallic halide. The cuprous and argentous complexes were found to be tetrameric whilst the gold complex was monomeric. The structure of tetrakis monoiodo triethylarsine copper I investigated by crystal structure analysis (Mann, Purdie and Wells, 1937a) showed that in the macro molecule each copper atom was tetrahedral by reason of iodine bridges, whilst each iodine atom was three covalent. The stability of the silver compound $[\text{Ag}.\text{IAs}(\text{C}_2\text{H}_5)_2]_4$ was much lower than the copper compound, and in solution extensive dissociation to the two covalent monomeric form occurred. Burrows and Parker (1933) found that the silver halide complexes with diphenylmethyl arsine and dimethylphenylarsine were highly insoluble, and of the form $\text{Ag}(\text{Ph}_2\text{MeAs})_2.\text{X}$. With boiling alcohol decomposition occurred with loss of arsine, but evidence was not found for the existence of complexes with only one molecule of arsine coordinated. Recent reinvestigation of these compounds (Dwyer and Savage, 1949) under a variety of conditions also failed to isolate compounds containing only one molecule of arsine. Since the insolubility of the compounds precluded molecular weight determinations, it is not possible to know whether the bis-arsine complexes are polymeric and contain four-covalent silver or are monomeric with the silver atom three-covalent. It is significant that Burrows and Sandford (1936), operating with the same two arsines, were able to isolate cuprous halide complexes which contained only one molecule of the arsine and were monomeric, suggesting that the type of arsine coordinated has some influence on the possibility of polymeric molecules.

The aurous halide complexes with tertiary arsines and phosphines were thoroughly studied by Mann and Purdie and Wells (1937b) and were found to be monomeric, of the type $\text{R}_3\text{As}.\text{Aux}$ ($\text{R}=\text{C}_2\text{H}_5$, C_3H_7 , C_4H_9 ; $\text{X}=\text{Cl}$, Br , I , CNS) and contained two covalent gold. Many of these compounds were notably stable, and could be distilled under vacuum.

In the present investigation it was thought valuable to determine whether the arsines used by Burrows and Sandford (*loc. cit.*) would yield the usual kind of gold complex, and whether a greater tendency to polymerisation would occur in the iodo than in the chloro compounds. The aurous chloride complexes were made by allowing two molecules of the arsine to react with one molecule of auric chloride in warm aqueous alcoholic solution when reduction and complex formation occurred rapidly.



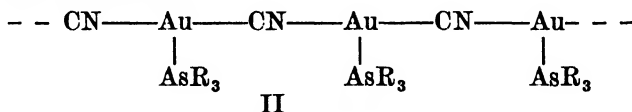
The bromo and iodo compounds were obtained by treatment of the chloro compound with potassium bromide and iodide.

The complexes after crystallisation from aqueous alcohol were obtained as fine white needles, with sharp melting points. Dilute solutions in benzene were monomeric and hence contained two-covalent gold, but the iodide showed a pronounced tendency towards association in concentrated solution. A 2.5% solution had almost doubled the calculated molecular weight and, if it is assumed that tetrameric molecules were formed, was nearly 40% associated into these macro molecules. It is evident that the stronger bonding power of the iodine atom has an important influence on the formation of associated molecules of the type described for the copper and silver complexes.

The coordination compounds of gold I, silver I and Copper I cyanides do not appear to have been investigated hitherto. They should be of special interest because of the linear —CN— bonds on the one hand and the high bonding power of the CN group on the other. Whilst silver and cuprous cyanide both dissolve in alcoholic solutions of tertiary arsines, and complex compounds are precipitated on dilution with water or evaporation of the solvent, they lose arsine so easily that they cannot be purified and ultimately decompose completely to the original cyanide (Dwyer and Savage, *loc. cit.*). With aurous cyanide and diphenyl methyl arsine two impure compounds could be obtained: $\text{AuCN} \cdot 2\text{Ph}_2\text{MeAs}$ I and $\text{AuCN} \cdot \text{Ph}_2\text{MeAs}$ II. The corresponding compounds with dimethyl phenyl arsine were obtained only as sticky gums and have not been investigated further.

The bis arsine complex I was obtained as a white crystalline substance, easily soluble in organic solvents to colourless solutions, which became yellow on standing or warming and deposited the monoarsine complex II as a pale yellow powder. In freezing bromoform I was dissociated to give a molecular weight almost half of the calculated value. One molecule of arsine was dissociated from the compound and could be easily detected by its odour. The compound I is considered to contain three-covalent gold. It is probable that the silver halide complexes containing two molecules of arsine described by Burrows and Parker (*loc. cit.*) are also three-covalent. It is significant that deposition of the yellow substance II did not occur except on warming, so that apparently a soluble two-covalent complex $\text{AuCN} \cdot \text{Ph}_2\text{MeAs}$ may exist in solution as an unstable compound. With excess arsine this compound apparently passes into I or alternatively passes into the yellow substance II, which from its insolubility in all solvents, including boiling nitrobenzene, is considered to be polymeric.

The substance II is formulated as containing three-covalent gold through an infinite chain of —Au—CN—Au—CN— groups. The ease of transformation of II into I by treatment with excess arsine, and the loss of arsine from II by continued boiling with organic solvents to yield almost pure aurous cyanide are consistent with this formulation.



An investigation is now being made of the aurous, cuprous and silver halide and cyanide complexes with diarsines such as ethylene bis-diphenyl arsine and ethylene bis phenylmethyl arsine, which should provide further evidence of the existence of three covalent complexes of these metals.

EXPERIMENTAL.

Auric chloride solution (50 mls.—1% with respect to Au) was mixed with alcohol (20 mls.) and heated to 50° C. The arsine (2 mols.) in alcohol (20 mls.) was added gradually to the warm gold solution with constant stirring. The yellow colour was soon discharged and a colourless

solution of the chloro complex resulted. The bromo or iodo complexes were formed by adding 5 mls. of 10% KBr or KI solution and keeping the solution warm for 10 minutes. Water was finally added until a permanent opalescence resulted—and the mixture allowed to cool slowly. The addition of a little petroleum ether dissolved traces of unreacted arsine and prevented the formation of gums or oils. The white crystalline products were crystallised from warm aqueous alcohol. The series prepared from PhMe_2As crystallised as needles, and from Ph_2MeAs as plates.

| | |
|--|--|
| $\text{PhMe}_2\text{As} \cdot \text{AuCl}$, m.p. 121°C . | $\text{Ph}_2\text{MeAs} \cdot \text{AuCl}$, m.p. 121°C . |
| $\text{PhMe}_2\text{As} \cdot \text{AuBr}$, m.p. 120.5°C . | $\text{Ph}_2\text{MeAs} \cdot \text{AuBr}$, m.p. 118.5°C . |
| $\text{PhMe}_2\text{As} \cdot \text{AuI}$, m.p. 130.5°C . | $\text{Ph}_2\text{MeAs} \cdot \text{AuI}$, m.p. 128°C . |

All were soluble in chloroform, benzene, acetone, sparingly soluble in petroleum ether and glacial acetic acid, and insoluble in water. Prolonged heating in any of these solvents led to decomposition and precipitation of gold. Dilute solutions in light became purple or brown, as do the crystals.

TABLE I.
Analytical Data.

| Compound. | Au. | | Halogen. | | C. | | H. | |
|---|--------|-------------|----------|-------------|--------|-------------|--------|-------------|
| | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. | Found. | Calculated. |
| $\text{PhMe}_2\text{As} \cdot \text{AuCl}$.. | 48.5 | 47.65 | 8.63 | 8.56 | 22.96 | 23.15 | 2.80 | 2.65 |
| $\text{PhMe}_2\text{As} \cdot \text{AuBr}$.. | 42.8 | 42.9 | 17.32 | 17.40 | 20.31 | 20.90 | 2.52 | 2.41 |
| $\text{PhMe}_2\text{As} \cdot \text{AuI}$.. | 39.15 | 39.0 | 24.53 | 25.15 | 19.09 | 18.98 | 2.30 | 2.18 |
| $\text{Ph}_2\text{MeAs} \cdot \text{AuCl}$.. | 41.0 | 41.4 | 7.53 | 7.45 | 32.85 | 32.75 | 2.87 | 2.72 |
| $\text{Ph}_2\text{MeAs} \cdot \text{AuBr}$.. | 37.0 | 37.8 | 15.48 | 15.37 | 30.50 | 30.00 | 2.63 | 2.49 |
| $\text{Ph}_2\text{MeAs} \cdot \text{AuI}$.. | 34.1 | 34.75 | 21.56 | 22.35 | 27.08 | 27.48 | 2.25 | 2.29 |

TABLE II.
Molecular Weights.

| | $\text{PhMe}_2\text{As} \cdot \text{AuI}$. | | | $\text{Ph}_2\text{MeAs} \cdot \text{AuCl}$. | | |
|-----------------------------------|---|--------|---------|--|--------|--------|
| Concentration | 0.025 M | 0.04 M | 0.051 M | 0.02 M | 0.07 M | 0.08 M |
| Molecular weight .. | 602 | 652 | 756 | 451 | 504 | 543 |
| Calculated molecular weight | — | 506 | — | — | 477 | — |

I. Bis-diphenyl Methyl Arsine Gold I Cyanide.

Auric chloride solution (50 mls.—1% with respect to Au) was treated with diphenylmethyl arsine (1.85 g.—3 mols.) in alcohol (30 mls.) followed by potassium cyanide (0.17 g.) dissolved in water (10 mls.). Water was then added in excess and the resulting white oil became solid on shaking with petroleum ether. It was recrystallised from aqueous alcohol containing a little arsine and the white crystals washed with a little petroleum ether. This washing could not be carried to completion without decomposing the compound. The substance melted at 91°C . It was soluble in benzene, chloroform, alcohol and acetone, but on heating in any of these solvents decomposed with the separation of the yellow form. The solid was unstable and gradually became yellow with the development of the odour of arsine.

Found: Au=29.2%, 26.6%; C=46.1%; H=3.8%. Molecular weight in bromoform from ebullioscopic measurements: 376, 441, 516 for 0.018 M, 0.03 M, 0.04 M solutions, respectively.

Calculated for $\text{AuCN} \cdot 2(\text{C}_6\text{H}_5)_2\text{CH}_2\text{As}$: Au=27.73%; C=45.5%; H=3.68%. Molecular weight=712.

II. Diphenylmethylarsine Gold I Cyanide.

This substance could be prepared like the compound above by using 2 mols. of arsine and warming the mixture or preferably by boiling I in benzene or alcohol solution. It could not be recrystallised, being insoluble in all solvents even in nitrobenzene. It dissolved in alcohol and arsine to form a colourless solution of I. On heating, the substance became viscous at about 85° C. and decomposed at about 280° C. The compound could not be obtained pure, as it appeared to be always contaminated with aurous cyanide. The latter substance could be isolated almost pure by very long boiling of II with bromobenzene.

Found: Au=84.46, 84.42%. Calculated for AuCN : Au=84.43%.

Found: Au=45.2, 46.7%. Calculated for $(\text{AuCN} \cdot (\text{C}_6\text{H}_5)_2\text{CH}_2\text{As})_n$: Au=42.20%.

SUMMARY.

Aurous halides react with diphenylmethylarsine and dimethylphenylarsine to yield complexes of the type $\text{AuX} \cdot \text{AsR}_3$. There is evidence of polymerisation of the iodo compound in concentrated solution—possibly due to the formation of tetrameric molecules. With aurous cyanide two complexes were obtained, a yellow, highly insoluble probably polymeric substance— $(\text{AuCN} \cdot \text{Ph}_2\text{MeAs})^*$ —and an unstable white substance containing two molecules of arsine in which the gold atom is three-covalent.

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KEPLER'S PROBLEM—THE PARABOLIC CASE.

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The solution of the parabolic case of Keplerian motion is given by

$$12\mu + \mu^3 = 12\sqrt{2}kq^{-3/2}t = D = 0.29192930q^{-3/2}t$$

where, in the notation of a former paper (Wood, 1950), $\mu = 2 \tan v/2$ and, with the constant given, t is in days. The solution of this equation is needed not only for the parabolic orbit but also to give a first approximation in the case of a nearly parabolic ellipse or hyperbola.

In order to disclose the range of variables for which solution is commonly necessary an examination was made of the orbits which do occur. The lists of comet orbits of Galle (1894), Chambers (1889 and 1909), Winlock (1896) and Crommelin (1925 and 1932) and the comet notes of current journals for 1931 to 1940 were examined.

Any tabulation naturally proceeds from perihelion ($t=0$) and carries on as far as the computer may think desirable. Two of the most convenient existing tables, those of Strömberg (1927) and Subbotin (1929), give $\tan v/2$ with argument $B(=tq^{-3/2})$ as far as $B=300$. From the above list those comets having parabolic or nearly parabolic orbits were selected which had been observed in a part of their orbit for which $B>300$. From this list was taken the only one (Halley's) for which the solution in the elliptical form becomes appropriate before B reaches 300—incidentally no comet with a hyperbolic orbit has been observed beyond the zone of applicability of the nearly parabolic solution. This left 36 comets for which a solution with $B>300$ was necessary, the extreme value of B corresponding to any observation being 377,000 for comet 1882 II.

There is a strong tendency for the average period of observation of comets to increase. The following table gives the average duration of visibility of comets (omitting Halley's and Schwassmam—Wachmann 1925 II). During successive twenty-year periods.

| Period. | Number of Comets. | Mean Duration of Visibility (in Days). |
|--------------------|-------------------|--|
| 1851 to 1870 | 76 | 75 |
| 1871 to 1890 | 92 | 95 |
| 1891 to 1910 | 94 | 115 |
| 1911 to 1930 | 103 | 131 |

This tendency continues, due to the effort of several observers, notably van Biesbroeck, to extend observed orbital arcs by the use of large telescopes.

The argument to be used for tables given here is D ($3.42 \dots D=B$) and the values of D corresponding to greatest observed distances from perihelion of the comets in the period 1851-1940 are distributed as follows :

| Max D . | Number of Comets. |
|----------------|-------------------|
| 100 to 200 .. | 14 |
| 200 to 400 .. | 6 |
| 400 to 1000 .. | 3 |
| > 1000 .. | 7 |

If we try to relate the period of visibility of comets to the perihelion distance we find that for perihelion distances from 0 to about 1.4 units the average duration remains nearly constant at about 90 days but with q between 1.6 and 2.0 units they have an average period of visibility of about 250 days which thereafter falls off.

In the circumstances large values of D are very probable for comets of small perihelion distance and all of the comets in the above list having max $D > 100$ have q small. Although the existing tables cover the majority of cases and it would be impracticable to give full tabulation as far as the extreme case, it is nevertheless desirable to have convenient processes to deal with any case that may occur, especially in view of the increased capacity to observe comets at great distances.

Below are tabulated two methods of solving the parabolic equation. Table 1 was formed by calculating approximate values of μ at ten times the interval of the table (except for small portions where five times was necessary) using the tables of Oppolzer (1886). These were corrected by an iterative process to give values accurate to two places beyond what is given in Table 1, differenced and subtabulated to the interval of the table. It is intended that errors will not exceed 0.52 unit of the last recorded place.

The first part of Table 1 gives μ to seven decimal places at interval 0.1 of D up to 100 and the second part ($100 < D < 1000$) at interval 1 gives μ to six decimals. The effect of the third difference being negligible throughout the table we may interpolate with the Newton-Gauss formula

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2}\delta^2\mu_0$$

where n is the fraction of the interval to be interpolated. $\delta^2\mu$ is given in Table 1 where it is appreciable and when linear interpolation is possible the first difference is tabulated. The coefficient of the second difference is given in the Critical Table on the interleaved flap.

There are two points for comment about this table. It would have been possible to form a table at a closer interval not requiring the use of second differences; but using a calculating machine with an easily accessible list of second difference coefficients involves very little more work (only a few seconds) than linear interpolation and the time for the determination of μ has already, by such a table as this, been reduced to only a small proportion of the time needed to produce one ephemeris place. The extra bulk of table required to avoid the use of second differences seems unjustifiable. Also, an argument much used in tables of parabolic motion is $tq^{-3/2}$, but, with $12\sqrt{2}kq^{-3/2}$ pre-computed for the orbit, the argument adopted here involves no extra time and

CRITICAL TABLE OF $n(1-n)/2$.

| n | $\frac{n(1-n)}{2}$ | n | n | $\frac{n(1-n)}{2}$ | n | n | $\frac{n(1-n)}{2}$ | n | n | $\frac{n(1-n)}{2}$ | n |
|--------|--------------------|--------|--------|--------------------|--------|--------|--------------------|--------|--------|--------------------|--------|
| 0.0000 | 0.000 | 1.0000 | 0.0675 | 0.032 | 0.9325 | 0.1492 | 0.064 | 0.8508 | 0.2571 | 0.096 | 0.7429 |
| .0010 | .001 | 0.9990 | .0698 | .033 | .9302 | .1521 | .065 | .8479 | .2612 | .097 | .7388 |
| .0030 | .002 | .9970 | .0722 | .034 | .9278 | .1550 | .066 | .8450 | .2654 | .098 | .7346 |
| .0050 | .003 | .9950 | .0745 | .035 | .9255 | .1579 | .067 | .8421 | .2697 | .099 | .7303 |
| .0070 | .004 | .9930 | .0769 | .036 | .9231 | .1608 | .068 | .8392 | .2741 | .100 | .7259 |
| .0090 | .005 | .9910 | .0792 | .037 | .9208 | .1638 | .069 | .8362 | .2786 | .101 | .7214 |
| .0111 | .006 | .9889 | .0816 | .038 | .9184 | .1668 | .070 | .8332 | .2832 | .102 | .7168 |
| .0131 | .007 | .9869 | .0840 | .039 | .9160 | .1698 | .071 | .8302 | .2878 | .103 | .7122 |
| .0152 | .008 | .9848 | .0864 | .040 | .9136 | .1728 | .072 | .8272 | .2926 | .104 | .7074 |
| .0172 | .009 | .9828 | .0889 | .041 | .9111 | .1759 | .073 | .8241 | .2975 | .105 | .7025 |
| .0193 | .010 | .9807 | .0913 | .042 | .9087 | .1790 | .074 | .8210 | .3025 | .106 | .6975 |
| .0214 | .011 | .9786 | .0937 | .043 | .9063 | .1821 | .075 | .8179 | .3076 | .107 | .6924 |
| .0235 | .012 | .9765 | .0962 | .044 | .9038 | .1853 | .076 | .8147 | .3129 | .108 | .6871 |
| .0256 | .013 | .9744 | .0987 | .045 | .9013 | .1885 | .077 | .8115 | .3183 | .109 | .6817 |
| .0277 | .014 | .9723 | .1012 | .046 | .8988 | .1917 | .078 | .8083 | .3239 | .110 | .6761 |
| .0298 | .015 | .9702 | .1037 | .047 | .8963 | .1950 | .079 | .8050 | .3297 | .111 | .6703 |
| .0320 | .016 | .9680 | .1062 | .048 | .8938 | .1983 | .080 | .8017 | .3356 | .112 | .6644 |
| .0341 | .017 | .9659 | .1088 | .049 | .8912 | .2016 | .081 | .7984 | .3418 | .113 | .6582 |
| .0363 | .018 | .9637 | .1114 | .050 | .8886 | .2050 | .082 | .7950 | .3483 | .114 | .6517 |
| .0384 | .019 | .9616 | .1139 | .051 | .8861 | .2084 | .083 | .7916 | .3550 | .115 | .6450 |
| .0406 | .020 | .9594 | .1165 | .052 | .8835 | .2119 | .084 | .7881 | .3621 | .116 | .6379 |
| .0428 | .021 | .9572 | .1192 | .053 | .8808 | .2153 | .085 | .7847 | .3696 | .117 | .6304 |
| .0450 | .022 | .9550 | .1218 | .054 | .8782 | .2189 | .086 | .7811 | .3775 | .118 | .6225 |
| .0472 | .023 | .9528 | .1245 | .055 | .8755 | .2225 | .087 | .7775 | .3859 | .119 | .6141 |
| .0494 | .024 | .9506 | .1271 | .056 | .8729 | .2261 | .088 | .7739 | .3951 | .120 | .6049 |
| .0516 | .025 | .9484 | .1298 | .057 | .8702 | .2298 | .089 | .7702 | .4051 | .121 | .5949 |
| .0539 | .026 | .9461 | .1325 | .058 | .8675 | .2335 | .090 | .7665 | .4163 | .122 | .5837 |
| .0561 | .027 | .9439 | .1353 | .059 | .8647 | .2373 | .091 | .7627 | .4292 | .123 | .5708 |
| .0584 | .028 | .9416 | .1380 | .060 | .8620 | .2411 | .092 | .7589 | .4452 | .124 | .5548 |
| .0606 | .029 | .9394 | .1408 | .061 | .8592 | .2450 | .093 | .7550 | .4683 | .125 | .5317 |
| .0629 | .030 | .9371 | .1436 | .062 | .8564 | .2490 | .094 | .7510 | .5316 | .124 | .4684 |
| .0652 | 0.031 | .9348 | .1464 | 0.063 | .8536 | .2530 | 0.095 | .7470 | .5547 | 0.123 | .4453 |
| 0.0675 | | 0.9325 | 0.1492 | | 0.8508 | 0.2571 | | 0.7429 | 0.5707 | | 0.4293 |

In critical cases take the value of $n(1-n)/2$ lying higher on the page.

$$\mu_n = (1-n)\mu_0 + n\mu_1 - \frac{n(1-n)}{2} \delta^2 \mu_0$$

$\delta^2 \mu_0$ is always negative.

TABLE 1.

| D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 |
|-----|------------|------------|------|------------|------------|------|------------|------------|------|------------|------------|
| 0.0 | 0.000 0000 | 0 | 5.0 | 0.410 8859 | 125 | 10.0 | 0.791 9429 | 178 | 15.0 | 1.129 8170 | 171 |
| 0.1 | 0.008 3333 | 3 | 5.1 | 0.418 8755 | 129 | 10.1 | 0.799 1378 | 178 | 15.1 | 1.136 1258 | 171 |
| 0.2 | 0.016 6663 | 6 | 5.2 | 0.426 8522 | 129 | 10.2 | 0.806 3149 | 177 | 15.2 | 1.142 4175 | 169 |
| 0.3 | 0.024 9987 | 9 | 5.3 | 0.434 8160 | 132 | 10.3 | 0.813 4743 | 180 | 15.3 | 1.148 6923 | 170 |
| 0.4 | 0.033 3302 | 11 | 5.4 | 0.442 7666 | 133 | 10.4 | 0.820 6157 | 177 | 15.4 | 1.154 9501 | 169 |
| 0.5 | 0.041 6606 | 14 | 5.5 | 0.450 7039 | 135 | 10.5 | 0.827 7394 | 180 | 15.5 | 1.161 1910 | 169 |
| 0.6 | 0.049 9896 | 18 | 5.6 | 0.458 6277 | 136 | 10.6 | 0.834 8451 | 179 | 15.6 | 1.167 4150 | 168 |
| 0.7 | 0.058 3168 | 20 | 5.7 | 0.466 5379 | 139 | 10.7 | 0.841 9329 | 179 | 15.7 | 1.173 6222 | 168 |
| 0.8 | 0.066 6420 | 23 | 5.8 | 0.474 4342 | 139 | 10.8 | 0.849 0028 | 179 | 15.8 | 1.179 8126 | 167 |
| 0.9 | 0.074 9649 | 26 | 5.9 | 0.482 3166 | 142 | 10.9 | 0.856 0548 | 180 | 15.9 | 1.185 9863 | 167 |
| 1.0 | 0.083 2852 | 29 | 6.0 | 0.490 1848 | 142 | 11.0 | 0.863 0888 | 179 | 16.0 | 1.192 1433 | 166 |
| 1.1 | 0.091 6026 | 31 | 6.1 | 0.498 0388 | 145 | 11.1 | 0.870 1049 | 180 | 16.1 | 1.198 2837 | 166 |
| 1.2 | 0.099 9169 | 35 | 6.2 | 0.505 8783 | 146 | 11.2 | 0.877 1030 | 179 | 16.2 | 1.204 4075 | 165 |
| 1.3 | 0.108 2277 | 37 | 6.3 | 0.513 7032 | 147 | 11.3 | 0.884 0832 | 181 | 16.3 | 1.210 5148 | 165 |
| 1.4 | 0.116 5348 | 40 | 6.4 | 0.521 5134 | 149 | 11.4 | 0.891 0453 | 179 | 16.4 | 1.216 6056 | 165 |
| 1.5 | 0.124 8379 | 43 | 6.5 | 0.529 3087 | 149 | 11.5 | 0.897 9895 | 179 | 16.5 | 1.222 6799 | 163 |
| 1.6 | 0.133 1367 | 46 | 6.6 | 0.537 0891 | 152 | 11.6 | 0.904 9158 | 181 | 16.6 | 1.228 7379 | 163 |
| 1.7 | 0.141 4309 | 48 | 6.7 | 0.544 8543 | 153 | 11.7 | 0.911 8240 | 179 | 16.7 | 1.234 7796 | 163 |
| 1.8 | 0.149 7203 | 51 | 6.8 | 0.552 6042 | 153 | 11.8 | 0.918 7143 | 179 | 16.8 | 1.240 8050 | 162 |
| 1.9 | 0.158 0046 | 54 | 6.9 | 0.560 3388 | 156 | 11.9 | 0.925 5867 | 181 | 16.9 | 1.246 8142 | 162 |
| 2.0 | 0.166 2835 | 56 | 7.0 | 0.568 0578 | 156 | 12.0 | 0.932 4410 | 178 | 17.0 | 1.252 8072 | 161 |
| 2.1 | 0.174 5568 | 60 | 7.1 | 0.575 7612 | 157 | 12.1 | 0.939 2775 | 180 | 17.1 | 1.258 7841 | 160 |
| 2.2 | 0.182 8241 | 62 | 7.2 | 0.583 4489 | 159 | 12.2 | 0.946 0960 | 179 | 17.2 | 1.264 7450 | 161 |
| 2.3 | 0.191 0852 | 64 | 7.3 | 0.591 1207 | 159 | 12.3 | 0.952 8966 | 180 | 17.3 | 1.270 6898 | 159 |
| 2.4 | 0.199 3399 | 67 | 7.4 | 0.598 7766 | 162 | 12.4 | 0.959 6792 | 178 | 17.4 | 1.276 6187 | 160 |
| 2.5 | 0.207 5879 | 70 | 7.5 | 0.606 4163 | 161 | 12.5 | 0.966 4440 | 179 | 17.5 | 1.282 5316 | 157 |
| 2.6 | 0.215 8289 | 73 | 7.6 | 0.614 0399 | 162 | 12.6 | 0.973 1909 | 179 | 17.6 | 1.288 4288 | 159 |
| 2.7 | 0.224 0626 | 75 | 7.7 | 0.621 6473 | 165 | 12.7 | 0.979 9199 | 178 | 17.7 | 1.294 3101 | 157 |
| 2.8 | 0.232 2888 | 77 | 7.8 | 0.629 2382 | 163 | 12.8 | 0.986 6311 | 179 | 17.8 | 1.300 1757 | 156 |
| 2.9 | 0.240 5073 | 80 | 7.9 | 0.636 8128 | 167 | 12.9 | 0.993 3244 | 177 | 17.9 | 1.306 0257 | 157 |
| 3.0 | 0.248 7178 | 82 | 8.0 | 0.644 3707 | 166 | 13.0 | 1.000 0000 | 178 | 18.0 | 1.311 8600 | 156 |
| 3.1 | 0.256 9201 | 85 | 8.1 | 0.651 9120 | 167 | 13.1 | 1.006 6578 | 178 | 18.1 | 1.317 6787 | 155 |
| 3.2 | 0.265 1139 | 88 | 8.2 | 0.659 4366 | 168 | 13.2 | 1.013 2978 | 177 | 18.2 | 1.323 4819 | 154 |
| 3.3 | 0.273 2989 | 90 | 8.3 | 0.666 9444 | 168 | 13.3 | 1.019 9201 | 177 | 18.3 | 1.329 2697 | 154 |
| 3.4 | 0.281 4749 | 91 | 8.4 | 0.674 4354 | 171 | 13.4 | 1.026 5247 | 177 | 18.4 | 1.335 0421 | 154 |
| 3.5 | 0.289 6418 | 95 | 8.5 | 0.681 9093 | 169 | 13.5 | 1.033 1116 | 176 | 18.5 | 1.340 7991 | 153 |
| 3.6 | 0.297 7992 | 97 | 8.6 | 0.689 3663 | 172 | 13.6 | 1.039 6809 | 176 | 18.6 | 1.346 5408 | 152 |
| 3.7 | 0.305 9469 | 99 | 8.7 | 0.696 8061 | 171 | 13.7 | 1.046 2326 | 176 | 18.7 | 1.352 2673 | 152 |
| 3.8 | 0.314 0847 | 102 | 8.8 | 0.704 2288 | 172 | 13.8 | 1.052 7667 | 176 | 18.8 | 1.357 9786 | 151 |
| 3.9 | 0.322 2123 | 103 | 8.9 | 0.711 6343 | 173 | 13.9 | 1.059 2832 | 175 | 18.9 | 1.363 6748 | 150 |
| 4.0 | 0.330 3296 | 106 | 9.0 | 0.719 0225 | 173 | 14.0 | 1.065 7822 | 174 | 19.0 | 1.369 3560 | 151 |
| 4.1 | 0.338 4363 | 108 | 9.1 | 0.726 3934 | 175 | 14.1 | 1.072 2638 | 175 | 19.1 | 1.375 0221 | 149 |
| 4.2 | 0.346 5322 | 110 | 9.2 | 0.733 7468 | 173 | 14.2 | 1.078 7279 | 175 | 19.2 | 1.380 6733 | 149 |
| 4.3 | 0.354 6171 | 112 | 9.3 | 0.741 0829 | 176 | 14.3 | 1.085 1745 | 173 | 19.3 | 1.386 3096 | 149 |
| 4.4 | 0.362 6908 | 114 | 9.4 | 0.748 4014 | 175 | 14.4 | 1.091 6038 | 173 | 19.4 | 1.391 9310 | 147 |
| 4.5 | 0.370 7531 | 117 | 9.5 | 0.755 7024 | 176 | 14.5 | 1.098 0158 | 173 | 19.5 | 1.397 5377 | 147 |
| 4.6 | 0.378 8037 | 118 | 9.6 | 0.762 9858 | 176 | 14.6 | 1.104 4105 | 173 | 19.6 | 1.403 1297 | 147 |
| 4.7 | 0.386 8425 | 120 | 9.7 | 0.770 2516 | 177 | 14.7 | 1.110 7879 | 172 | 19.7 | 1.408 7070 | 146 |
| 4.8 | 0.394 8693 | 123 | 9.8 | 0.777 4997 | 176 | 14.8 | 1.117 1481 | 172 | 19.8 | 1.414 2697 | 146 |
| 4.9 | 0.402 8838 | 124 | 9.9 | 0.784 7302 | 178 | 14.9 | 1.123 4911 | 171 | 19.9 | 1.419 8178 | 144 |
| 5.0 | 0.410 8859 | 125 | 10.0 | 0.791 9429 | 178 | 15.0 | 1.129 8170 | 171 | 20.0 | 1.425 3515 | 145 |

TABLE 1.

| D | μ | δ^a | D | μ | δ^a | D | μ | δ^a | D | μ | δ^a |
|------|------------|------------|------|------------|------------|------|------------|------------|------|------------|------------|
| 20.0 | 1.425 3515 | 145 | 25.0 | 1.684 8004 | 116 | 30.0 | 1.914 8811 | 95 | 35.0 | 2.121 2503 | 76 |
| 20.1 | 1.430 8707 | 144 | 25.1 | 1.689 6689 | 116 | 30.1 | 1.919 2241 | 93 | 35.1 | 2.125 1682 | 77 |
| 20.2 | 1.436 3755 | 142 | 25.2 | 1.694 5258 | 117 | 30.2 | 1.923 5578 | 95 | 35.2 | 2.129 0784 | 76 |
| 20.3 | 1.441 8661 | 144 | 25.3 | 1.699 3710 | 116 | 30.3 | 1.927 8820 | 92 | 35.3 | 2.132 9810 | 75 |
| 20.4 | 1.447 3423 | 141 | 25.4 | 1.704 2046 | 114 | 30.4 | 1.932 1970 | 93 | 35.4 | 2.136 8761 | 77 |
| 20.5 | 1.452 8044 | 142 | 25.5 | 1.709 0288 | 115 | 30.5 | 1.936 5027 | 93 | 35.5 | 2.140 7635 | 74 |
| 20.6 | 1.458 2523 | 141 | 25.6 | 1.713 8375 | 114 | 30.6 | 1.940 7991 | 91 | 35.6 | 2.144 6435 | 76 |
| 20.7 | 1.463 6861 | 141 | 25.7 | 1.718 6368 | 114 | 30.7 | 1.945 0864 | 93 | 35.7 | 2.148 5159 | 74 |
| 20.8 | 1.469 1058 | 139 | 25.8 | 1.723 4247 | 113 | 30.8 | 1.949 3644 | 90 | 35.8 | 2.152 3809 | 74 |
| 20.9 | 1.474 5116 | 139 | 25.9 | 1.728 2013 | 112 | 30.9 | 1.953 6334 | 92 | 35.9 | 2.156 2385 | 75 |
| 21.0 | 1.479 9035 | 139 | 26.0 | 1.732 9667 | 113 | 31.0 | 1.957 8932 | 90 | 36.0 | 2.160 0886 | 73 |
| 21.1 | 1.485 2815 | 138 | 26.1 | 1.737 7208 | 111 | 31.1 | 1.962 1440 | 90 | 36.1 | 2.163 9314 | 74 |
| 21.2 | 1.490 6457 | 137 | 26.2 | 1.742 4638 | 111 | 31.2 | 1.966 3858 | 90 | 36.2 | 2.167 7688 | 73 |
| 21.3 | 1.495 9962 | 138 | 26.3 | 1.747 1957 | 111 | 31.3 | 1.970 6186 | 90 | 36.3 | 2.171 5949 | 72 |
| 21.4 | 1.501 3329 | 136 | 26.4 | 1.751 9165 | 110 | 31.4 | 1.974 8424 | 88 | 36.4 | 2.175 4158 | 74 |
| 21.5 | 1.506 6560 | 136 | 26.5 | 1.756 6263 | 110 | 31.5 | 1.979 0574 | 89 | 36.5 | 2.179 2293 | 71 |
| 21.6 | 1.511 9655 | 135 | 26.6 | 1.761 3251 | 109 | 31.6 | 1.983 2635 | 88 | 36.6 | 2.183 0357 | 73 |
| 21.7 | 1.517 2615 | 134 | 26.7 | 1.766 0130 | 109 | 31.7 | 1.987 4608 | 88 | 36.7 | 2.186 8348 | 72 |
| 21.8 | 1.522 5441 | 135 | 26.8 | 1.770 6900 | 109 | 31.8 | 1.991 6493 | 88 | 36.8 | 2.190 6267 | 71 |
| 21.9 | 1.527 8132 | 133 | 26.9 | 1.775 3561 | 107 | 31.9 | 1.995 8290 | 87 | 36.9 | 2.194 4115 | 71 |
| 22.0 | 1.533 0890 | 134 | 27.0 | 1.780 0115 | 107 | 32.0 | 2.000 0000 | 87 | 37.0 | 2.198 1892 | 71 |
| 22.1 | 1.538 3114 | 132 | 27.1 | 1.784 6562 | 108 | 32.1 | 2.004 1623 | 86 | 37.1 | 2.201 9598 | 70 |
| 22.2 | 1.543 5406 | 132 | 27.2 | 1.789 2901 | 105 | 32.2 | 2.008 3160 | 86 | 37.2 | 2.205 7234 | 71 |
| 22.3 | 1.548 7566 | 131 | 27.3 | 1.793 9135 | 107 | 32.3 | 2.012 4611 | 86 | 37.3 | 2.209 4799 | 70 |
| 22.4 | 1.553 9695 | 131 | 27.4 | 1.798 5262 | 106 | 32.4 | 2.016 5976 | 85 | 37.4 | 2.213 2294 | 70 |
| 22.5 | 1.559 1493 | 130 | 27.5 | 1.803 1283 | 104 | 32.5 | 2.020 7256 | 86 | 37.5 | 2.216 9719 | 70 |
| 22.6 | 1.564 3261 | 131 | 27.6 | 1.807 7200 | 105 | 32.6 | 2.024 8450 | 84 | 37.6 | 2.220 7074 | 68 |
| 22.7 | 1.569 4898 | 128 | 27.7 | 1.812 3012 | 105 | 32.7 | 2.028 9560 | 84 | 37.7 | 2.224 4361 | 70 |
| 22.8 | 1.574 6407 | 129 | 27.8 | 1.816 8719 | 103 | 32.8 | 2.033 0586 | 84 | 37.8 | 2.228 1578 | 68 |
| 22.9 | 1.579 7787 | 128 | 27.9 | 1.821 4323 | 103 | 32.9 | 2.037 1528 | 84 | 37.9 | 2.231 8727 | 69 |
| 23.0 | 1.584 9039 | 127 | 28.0 | 1.825 9824 | 104 | 33.0 | 2.041 2386 | 83 | 38.0 | 2.235 5807 | 68 |
| 23.1 | 1.590 0164 | 128 | 28.1 | 1.830 5221 | 101 | 33.1 | 2.045 3161 | 83 | 38.1 | 2.239 2819 | 68 |
| 23.2 | 1.595 1161 | 126 | 28.2 | 1.835 0517 | 103 | 33.2 | 2.049 3853 | 83 | 38.2 | 2.242 9763 | 68 |
| 23.3 | 1.600 2032 | 125 | 28.3 | 1.839 5710 | 101 | 33.3 | 2.053 4462 | 82 | 38.3 | 2.246 6639 | 67 |
| 23.4 | 1.605 2778 | 127 | 28.4 | 1.844 0802 | 101 | 33.4 | 2.057 4989 | 82 | 38.4 | 2.250 3448 | 67 |
| 23.5 | 1.610 3397 | 124 | 28.5 | 1.848 5793 | 101 | 33.5 | 2.061 5434 | 82 | 38.5 | 2.254 0190 | 67 |
| 23.6 | 1.615 3892 | 124 | 28.6 | 1.853 0683 | 100 | 33.6 | 2.065 5797 | 80 | 38.6 | 2.257 6865 | 67 |
| 23.7 | 1.620 4263 | 125 | 28.7 | 1.857 5473 | 100 | 33.7 | 2.069 6080 | 82 | 38.7 | 2.261 3473 | 66 |
| 23.8 | 1.625 4509 | 122 | 28.8 | 1.862 0163 | 100 | 33.8 | 2.073 6281 | 80 | 38.8 | 2.265 0015 | 67 |
| 23.9 | 1.630 4633 | 124 | 28.9 | 1.866 4753 | 98 | 33.9 | 2.077 6402 | 81 | 38.9 | 2.268 6490 | 65 |
| 24.0 | 1.635 4633 | 121 | 29.0 | 1.870 9245 | 99 | 34.0 | 2.081 6442 | 79 | 39.0 | 2.272 2900 | 65 |
| 24.1 | 1.640 4512 | 122 | 29.1 | 1.875 3638 | 98 | 34.1 | 2.085 6403 | 80 | 39.1 | 2.275 9245 | 67 |
| 24.2 | 1.645 4269 | 122 | 29.2 | 1.879 7933 | 98 | 34.2 | 2.089 6284 | 80 | 39.2 | 2.279 5523 | 64 |
| 24.3 | 1.650 3904 | 120 | 29.3 | 1.884 2130 | 97 | 34.3 | 2.093 6085 | 78 | 39.3 | 2.283 1737 | 65 |
| 24.4 | 1.655 3419 | 120 | 29.4 | 1.888 6230 | 97 | 34.4 | 2.097 5808 | 79 | 39.4 | 2.286 7886 | 65 |
| 24.5 | 1.660 2814 | 119 | 29.5 | 1.893 0233 | 96 | 34.5 | 2.101 5452 | 79 | 39.5 | 2.290 3970 | 64 |
| 24.6 | 1.665 2090 | 120 | 29.6 | 1.897 4140 | 96 | 34.6 | 2.105 5017 | 77 | 39.6 | 2.293 9990 | 65 |
| 24.7 | 1.670 1246 | 119 | 29.7 | 1.901 7951 | 96 | 34.7 | 2.109 4505 | 78 | 39.7 | 2.297 5945 | 63 |
| 24.8 | 1.675 0283 | 117 | 29.8 | 1.906 1666 | 95 | 34.8 | 2.113 3915 | 77 | 39.8 | 2.301 1837 | 64 |
| 24.9 | 1.679 9203 | 119 | 29.9 | 1.910 5286 | 95 | 34.9 | 2.117 3248 | 78 | 39.9 | 2.304 7665 | 63 |
| 25.0 | 1.684 8004 | 116 | 30.0 | 1.914 8811 | 95 | 35.0 | 2.121 2503 | 76 | 40.0 | 2.308 3430 | 64 |

TABLE I.

| D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 |
|------|------------|------------|------|------------|------------|------|------------|------------|------|------------|------------|
| 40.0 | 2.308 3430 | 64 | 45.0 | 2.479 5733 | 53 | 50.0 | 2.637 5754 | 45 | 55.0 | 2.784 4020 | 38 |
| 40.1 | 2.311 9131 | 62 | 45.1 | 2.482 8553 | 53 | 50.1 | 2.640 6154 | 44 | 55.1 | 2.787 2363 | 38 |
| 40.2 | 2.315 4770 | 63 | 45.2 | 2.486 1320 | 52 | 50.2 | 2.643 6510 | 44 | 55.2 | 2.790 0668 | 38 |
| 40.3 | 2.319 0346 | 63 | 45.3 | 2.489 4035 | 52 | 50.3 | 2.646 6822 | 45 | 55.3 | 2.792 8935 | 38 |
| 40.4 | 2.322 5859 | 62 | 45.4 | 2.492 6698 | 52 | 50.4 | 2.649 7089 | 43 | 55.4 | 2.795 7164 | 38 |
| 40.5 | 2.326 1310 | 62 | 45.5 | 2.495 9309 | 52 | 50.5 | 2.652 7313 | 45 | 55.5 | 2.798 5355 | 37 |
| 40.6 | 2.329 6699 | 62 | 45.6 | 2.499 1868 | 51 | 50.6 | 2.655 7492 | 43 | 55.6 | 2.801 3509 | 37 |
| 40.7 | 2.333 2026 | 61 | 45.7 | 2.502 4376 | 52 | 50.7 | 2.658 7628 | 44 | 55.7 | 2.804 1626 | 38 |
| 40.8 | 2.336 7292 | 62 | 45.8 | 2.505 6832 | 52 | 50.8 | 2.661 7720 | 43 | 55.8 | 2.806 9705 | 37 |
| 40.9 | 2.340 2496 | 61 | 45.9 | 2.508 9236 | 50 | 50.9 | 2.664 7769 | 43 | 55.9 | 2.809 7747 | 37 |
| 41.0 | 2.343 7639 | 60 | 46.0 | 2.512 1590 | 51 | 51.0 | 2.667 7775 | 44 | 56.0 | 2.812 5752 | 38 |
| 41.1 | 2.347 2722 | 62 | 46.1 | 2.515 3893 | 51 | 51.1 | 2.670 7737 | 42 | 56.1 | 2.815 3719 | 36 |
| 41.2 | 2.350 7743 | 59 | 46.2 | 2.518 6145 | 51 | 51.2 | 2.673 7657 | 44 | 56.2 | 2.818 1650 | 36 |
| 41.3 | 2.354 2705 | 61 | 46.3 | 2.521 8346 | 50 | 51.3 | 2.676 7533 | 42 | 56.3 | 2.820 9545 | 38 |
| 41.4 | 2.357 7606 | 60 | 46.4 | 2.525 0497 | 50 | 51.4 | 2.679 7367 | 43 | 56.4 | 2.823 7402 | 36 |
| 41.5 | 2.361 2447 | 60 | 46.5 | 2.528 2598 | 51 | 51.5 | 2.682 7158 | 42 | 56.5 | 2.826 5223 | 36 |
| 41.6 | 2.364 7228 | 59 | 46.6 | 2.531 4648 | 49 | 51.6 | 2.685 6907 | 42 | 56.6 | 2.829 3008 | 37 |
| 41.7 | 2.368 1950 | 60 | 46.7 | 2.534 6649 | 50 | 51.7 | 2.688 6614 | 43 | 56.7 | 2.832 0756 | 36 |
| 41.8 | 2.371 6612 | 58 | 46.8 | 2.537 8600 | 49 | 51.8 | 2.691 6278 | 42 | 56.8 | 2.834 8468 | 36 |
| 41.9 | 2.375 1216 | 60 | 46.9 | 2.541 0502 | 50 | 51.9 | 2.694 5900 | 42 | 56.9 | 2.837 6144 | 37 |
| 42.0 | 2.378 5760 | 58 | 47.0 | 2.544 2354 | 49 | 52.0 | 2.697 5480 | 41 | 57.0 | 2.840 3783 | 35 |
| 42.1 | 2.382 0246 | 59 | 47.1 | 2.547 4157 | 50 | 52.1 | 2.700 5019 | 43 | 57.1 | 2.843 1387 | 36 |
| 42.2 | 2.385 4673 | 58 | 47.2 | 2.550 5910 | 48 | 52.2 | 2.703 4515 | 40 | 57.2 | 2.845 8955 | 35 |
| 42.3 | 2.388 9042 | 58 | 47.3 | 2.553 7615 | 48 | 52.3 | 2.706 3971 | 43 | 57.3 | 2.848 6488 | 36 |
| 42.4 | 2.392 3353 | 58 | 47.4 | 2.556 9272 | 50 | 52.4 | 2.709 3384 | 40 | 57.4 | 2.851 3985 | 36 |
| 42.5 | 2.395 7606 | 57 | 47.5 | 2.560 0879 | 47 | 52.5 | 2.712 2757 | 42 | 57.5 | 2.854 1446 | 35 |
| 42.6 | 2.399 1802 | 58 | 47.6 | 2.563 2439 | 49 | 52.6 | 2.715 2088 | 40 | 57.6 | 2.856 8872 | 36 |
| 42.7 | 2.402 5940 | 57 | 47.7 | 2.566 3950 | 48 | 52.7 | 2.718 1379 | 42 | 57.7 | 2.859 6262 | 34 |
| 42.8 | 2.406 0021 | 57 | 47.8 | 2.569 5413 | 48 | 52.8 | 2.721 0628 | 40 | 57.8 | 2.862 3618 | 36 |
| 42.9 | 2.409 4045 | 57 | 47.9 | 2.572 6828 | 48 | 52.9 | 2.723 9837 | 41 | 57.9 | 2.865 0938 | 35 |
| 43.0 | 2.412 8012 | 57 | 48.0 | 2.575 8195 | 47 | 53.0 | 2.726 9005 | 41 | 58.0 | 2.867 8223 | 34 |
| 43.1 | 2.416 1922 | 56 | 48.1 | 2.578 9515 | 48 | 53.1 | 2.729 8132 | 40 | 58.1 | 2.870 5474 | 36 |
| 43.2 | 2.419 5776 | 56 | 48.2 | 2.582 0787 | 47 | 53.2 | 2.732 7219 | 40 | 58.2 | 2.873 2689 | 34 |
| 43.3 | 2.422 9574 | 56 | 48.3 | 2.585 2012 | 47 | 53.3 | 2.735 6266 | 40 | 58.3 | 2.875 9870 | 34 |
| 43.4 | 2.426 3316 | 56 | 48.4 | 2.588 3190 | 47 | 53.4 | 2.738 5273 | 40 | 58.4 | 2.878 7017 | 35 |
| 43.5 | 2.429 7002 | 55 | 48.5 | 2.591 4321 | 47 | 53.5 | 2.741 4240 | 41 | 58.5 | 2.881 4129 | 35 |
| 43.6 | 2.433 0633 | 56 | 48.6 | 2.594 5405 | 46 | 53.6 | 2.744 3166 | 38 | 58.6 | 2.884 1206 | 34 |
| 43.7 | 2.436 4208 | 55 | 48.7 | 2.597 6443 | 47 | 53.7 | 2.747 2054 | 41 | 58.7 | 2.886 8249 | 34 |
| 43.8 | 2.439 7728 | 55 | 48.8 | 2.600 7434 | 47 | 53.8 | 2.750 0901 | 39 | 58.8 | 2.889 5258 | 34 |
| 43.9 | 2.443 1193 | 55 | 48.9 | 2.603 8378 | 45 | 53.9 | 2.752 9709 | 40 | 58.9 | 2.892 2233 | 34 |
| 44.0 | 2.446 4603 | 54 | 49.0 | 2.606 9277 | 47 | 54.0 | 2.755 8477 | 39 | 59.0 | 2.894 9174 | 34 |
| 44.1 | 2.449 7959 | 55 | 49.1 | 2.610 0129 | 45 | 54.1 | 2.758 7206 | 39 | 59.1 | 2.897 6081 | 34 |
| 44.2 | 2.453 1260 | 54 | 49.2 | 2.613 0936 | 46 | 54.2 | 2.761 5896 | 39 | 59.2 | 2.900 2954 | 38 |
| 44.3 | 2.456 4507 | 54 | 49.3 | 2.616 1697 | 46 | 54.3 | 2.764 4547 | 39 | 59.3 | 2.902 9794 | 34 |
| 44.4 | 2.459 7700 | 54 | 49.4 | 2.619 2412 | 45 | 54.4 | 2.767 3159 | 39 | 59.4 | 2.905 6600 | 34 |
| 44.5 | 2.463 0839 | 54 | 49.5 | 2.622 3082 | 46 | 54.5 | 2.770 1732 | 38 | 59.5 | 2.908 3372 | 33 |
| 44.6 | 2.466 3924 | 53 | 49.6 | 2.625 3706 | 45 | 54.6 | 2.773 0267 | 39 | 59.6 | 2.911 0111 | 33 |
| 44.7 | 2.469 6956 | 53 | 49.7 | 2.628 4285 | 44 | 54.7 | 2.775 8763 | 39 | 59.7 | 2.913 6817 | 34 |
| 44.8 | 2.472 9935 | 54 | 49.8 | 2.631 4820 | 46 | 54.8 | 2.778 7220 | 38 | 59.8 | 2.916 3489 | 33 |
| 44.9 | 2.476 2860 | 52 | 49.9 | 2.634 5309 | 44 | 54.9 | 2.781 5639 | 38 | 59.9 | 2.919 0128 | 32 |
| 45.0 | 2.479 5733 | 53 | 50.0 | 2.637 5754 | 45 | 55.0 | 2.784 4020 | 38 | 60.0 | 2.921 6735 | 34 |

TABLE 1.

| D | μ | δ^a | D | μ | δ^a | D | μ | δ^a | D | μ | δ^a |
|------|-------|------------|------|-------|------------|------|-------|------------|------|-------|------------|
| 60.0 | 2.921 | 8735 34 | 65.0 | 3.050 | 6859 30 | 70.0 | 3.172 | 4896 26 | 75.0 | 3.287 | 9463 21 |
| 60.1 | 2.924 | 3308 33 | 65.1 | 3.053 | 1894 28 | 70.1 | 3.174 | 8583 25 | 75.1 | 3.290 | 1959 24 |
| 60.2 | 2.926 | 9848 32 | 65.2 | 3.055 | 6901 28 | 70.2 | 3.177 | 2245 25 | 75.2 | 3.292 | 4431 21 |
| 60.3 | 2.929 | 6356 33 | 65.3 | 3.058 | 1880 30 | 70.3 | 3.179 | 5882 25 | 75.3 | 3.294 | 6882 23 |
| 60.4 | 2.932 | 2831 33 | 65.4 | 3.060 | 6829 27 | 70.4 | 3.181 | 9494 25 | 75.4 | 3.296 | 9310 22 |
| 60.5 | 2.934 | 9273 32 | 65.5 | 3.063 | 1751 29 | 70.5 | 3.184 | 3081 26 | 75.5 | 3.299 | 1716 23 |
| 60.6 | 2.937 | 5683 33 | 65.6 | 3.065 | 6644 29 | 70.6 | 3.186 | 6642 24 | 75.6 | 3.301 | 4099 22 |
| 60.7 | 2.940 | 2060 31 | 65.7 | 3.068 | 1508 27 | 70.7 | 3.189 | 0179 26 | 75.7 | 3.303 | 6460 21 |
| 60.8 | 2.942 | 8406 33 | 65.8 | 3.070 | 6345 29 | 70.8 | 3.191 | 3690 24 | 75.8 | 3.305 | 8800 23 |
| 60.9 | 2.945 | 4719 33 | 65.9 | 3.073 | 1153 28 | 70.9 | 3.193 | 7177 25 | 75.9 | 3.308 | 1117 22 |
| 61.0 | 2.948 | 0999 31 | 66.0 | 3.075 | 5933 28 | 71.0 | 3.196 | 0639 24 | 76.0 | 3.310 | 3412 22 |
| 61.1 | 2.950 | 7248 32 | 66.1 | 3.078 | 0685 28 | 71.1 | 3.198 | 4077 26 | 76.1 | 3.312 | 5685 22 |
| 61.2 | 2.953 | 3465 32 | 66.2 | 3.080 | 5409 28 | 71.2 | 3.200 | 7489 24 | 76.2 | 3.314 | 7936 22 |
| 61.3 | 2.955 | 9650 32 | 66.3 | 3.083 | 0105 27 | 71.3 | 3.203 | 0877 24 | 76.3 | 3.317 | 0165 21 |
| 61.4 | 2.958 | 5803 32 | 66.4 | 3.085 | 4774 28 | 71.4 | 3.205 | 4241 25 | 76.4 | 3.319 | 2373 23 |
| 61.5 | 2.961 | 1924 31 | 66.5 | 3.087 | 9415 28 | 71.5 | 3.207 | 7580 24 | 76.5 | 3.321 | 4558 21 |
| 61.6 | 2.963 | 8014 32 | 66.6 | 3.090 | 4028 28 | 71.6 | 3.210 | 0895 25 | 76.6 | 3.323 | 6722 21 |
| 61.7 | 2.966 | 4072 31 | 66.7 | 3.092 | 8613 27 | 71.7 | 3.212 | 4185 24 | 76.7 | 3.325 | 8865 23 |
| 61.8 | 2.969 | 0099 31 | 66.8 | 3.095 | 3171 28 | 71.8 | 3.214 | 7451 25 | 76.8 | 3.328 | 0985 21 |
| 61.9 | 2.971 | 6095 32 | 66.9 | 3.097 | 7701 27 | 71.9 | 3.217 | 0692 23 | 76.9 | 3.330 | 3084 21 |
| 62.0 | 2.974 | 2059 31 | 67.0 | 3.100 | 2204 27 | 72.0 | 3.219 | 3910 25 | 77.0 | 3.332 | 5162 22 |
| 62.1 | 2.976 | 7992 31 | 67.1 | 3.102 | 6680 28 | 72.1 | 3.221 | 7103 24 | 77.1 | 3.334 | 7218 21 |
| 62.2 | 2.979 | 3894 31 | 67.2 | 3.105 | 1128 26 | 72.2 | 3.224 | 0272 23 | 77.2 | 3.336 | 9253 22 |
| 62.3 | 2.981 | 9765 31 | 67.3 | 3.107 | 5550 28 | 72.3 | 3.226 | 3418 25 | 77.3 | 3.339 | 1266 21 |
| 62.4 | 2.984 | 5605 31 | 67.4 | 3.109 | 9944 27 | 72.4 | 3.228 | 6539 24 | 77.4 | 3.341 | 3258 22 |
| 62.5 | 2.987 | 1414 31 | 67.5 | 3.112 | 4311 27 | 72.5 | 3.230 | 9636 23 | 77.5 | 3.343 | 5228 20 |
| 62.6 | 2.989 | 7192 30 | 67.6 | 3.114 | 8651 27 | 72.6 | 3.233 | 2710 24 | 77.6 | 3.345 | 7178 22 |
| 62.7 | 2.992 | 2940 31 | 67.7 | 3.117 | 2964 26 | 72.7 | 3.235 | 5760 24 | 77.7 | 3.347 | 9106 21 |
| 62.8 | 2.994 | 8657 30 | 67.8 | 3.119 | 7251 28 | 72.8 | 3.237 | 8786 24 | 77.8 | 3.350 | 1013 21 |
| 62.9 | 2.997 | 4344 31 | 67.9 | 3.122 | 1510 26 | 72.9 | 3.240 | 1788 24 | 77.9 | 3.352 | 2899 22 |
| 63.0 | 3.000 | 0000 30 | 68.0 | 3.124 | 5743 27 | 73.0 | 3.242 | 4766 22 | 78.0 | 3.354 | 4763 20 |
| 63.1 | 3.002 | 5626 31 | 68.1 | 3.126 | 9949 26 | 73.1 | 3.244 | 7722 25 | 78.1 | 3.356 | 6607 21 |
| 63.2 | 3.005 | 1221 29 | 68.2 | 3.129 | 4129 27 | 73.2 | 3.247 | 0653 23 | 78.2 | 3.358 | 8430 21 |
| 63.3 | 3.007 | 6787 31 | 68.3 | 3.131 | 8282 26 | 73.3 | 3.249 | 3561 23 | 78.3 | 3.361 | 0232 21 |
| 63.4 | 3.010 | 2322 29 | 68.4 | 3.134 | 2409 27 | 73.4 | 3.251 | 6446 24 | 78.4 | 3.363 | 2013 21 |
| 63.5 | 3.012 | 7828 31 | 68.5 | 3.136 | 6509 25 | 73.5 | 3.253 | 9307 22 | 78.5 | 3.365 | 3773 20 |
| 63.6 | 3.015 | 3303 30 | 68.6 | 3.139 | 0584 28 | 73.6 | 3.256 | 2146 25 | 78.6 | 3.367 | 5513 21 |
| 63.7 | 3.017 | 8748 29 | 68.7 | 3.141 | 4631 25 | 73.7 | 3.258 | 4960 22 | 78.7 | 3.369 | 7232 21 |
| 63.8 | 3.020 | 4164 30 | 68.8 | 3.143 | 8653 26 | 73.8 | 3.260 | 7752 23 | 78.8 | 3.371 | 8930 21 |
| 63.9 | 3.022 | 9550 29 | 68.9 | 3.146 | 2649 27 | 73.9 | 3.263 | 0621 24 | 78.9 | 3.374 | 0607 20 |
| 64.0 | 3.025 | 4907 31 | 69.0 | 3.148 | 6618 25 | 74.0 | 3.265 | 3266 23 | 79.0 | 3.376 | 2264 21 |
| 64.1 | 3.028 | 0233 28 | 69.1 | 3.151 | 0562 26 | 74.1 | 3.267 | 5988 22 | 79.1 | 3.378 | 3900 20 |
| 64.2 | 3.030 | 5531 30 | 69.2 | 3.153 | 4480 27 | 74.2 | 3.269 | 8688 23 | 79.2 | 3.380 | 5516 21 |
| 64.3 | 3.033 | 0799 30 | 69.3 | 3.155 | 8371 25 | 74.3 | 3.272 | 1365 24 | 79.3 | 3.382 | 7111 20 |
| 64.4 | 3.035 | 6037 28 | 69.4 | 3.158 | 2237 25 | 74.4 | 3.274 | 4018 22 | 79.4 | 3.384 | 8686 20 |
| 64.5 | 3.038 | 1247 30 | 69.5 | 3.160 | 6078 27 | 74.5 | 3.276 | 6649 23 | 79.5 | 3.387 | 0241 21 |
| 64.6 | 3.040 | 6427 28 | 69.6 | 3.162 | 9892 24 | 74.6 | 3.278 | 9257 22 | 79.6 | 3.389 | 1775 20 |
| 64.7 | 3.043 | 1579 30 | 69.7 | 3.165 | 3682 27 | 74.7 | 3.281 | 1843 23 | 79.7 | 3.391 | 3289 20 |
| 64.8 | 3.045 | 6701 29 | 69.8 | 3.167 | 7445 25 | 74.8 | 3.283 | 4406 23 | 79.8 | 3.393 | 4783 21 |
| 64.9 | 3.048 | 1794 28 | 69.9 | 3.170 | 1183 25 | 74.9 | 3.285 | 6946 23 | 79.9 | 3.395 | 6256 19 |
| 65.0 | 3.050 | 6859 30 | 70.0 | 3.172 | 4896 26 | 75.0 | 3.287 | 9463 21 | 80.0 | 3.397 | 7710 21 |

TABLE 1.

| D | μ | δ^* | D | μ | δ^* | D | μ | δ^* | D | μ | δ^* |
|------|------------|------------|------|------------|------------|------|------------|------------|-------|------------|------------|
| 80.0 | 3.397 7710 | 21 | 85.0 | 3.502 5627 | 18 | 90.0 | 3.602 8285 | 17 | 95.0 | 3.699 0011 | 14 |
| 80.1 | 3.399 9143 | 20 | 85.1 | 3.504 6108 | 18 | 90.1 | 3.604 7907 | 16 | 95.1 | 3.700 8855 | 16 |
| 80.2 | 3.402 0556 | 19 | 85.2 | 3.506 6571 | 18 | 90.2 | 3.606 7513 | 16 | 95.2 | 3.702 7683 | 14 |
| 80.3 | 3.404 1950 | 21 | 85.3 | 3.508 7016 | 18 | 90.3 | 3.608 7103 | 17 | 95.3 | 3.704 6497 | 15 |
| 80.4 | 3.406 3323 | 20 | 85.4 | 3.510 7443 | 17 | 90.4 | 3.610 6676 | 15 | 95.4 | 3.706 5296 | 15 |
| 80.5 | 3.408 4676 | 19 | 85.5 | 3.512 7853 | 19 | 90.5 | 3.612 6234 | 17 | 95.5 | 3.708 4080 | 14 |
| 80.6 | 3.410 6010 | 21 | 85.6 | 3.514 8244 | 18 | 90.6 | 3.614 5775 | 16 | 95.6 | 3.710 2850 | 15 |
| 80.7 | 3.412 7323 | 19 | 85.7 | 3.516 8617 | 17 | 90.7 | 3.616 5300 | 17 | 95.7 | 3.712 1605 | 15 |
| 80.8 | 3.414 8617 | 20 | 85.8 | 3.518 8973 | 18 | 90.8 | 3.618 4808 | 15 | 95.8 | 3.714 0345 | 14 |
| 80.9 | 3.416 9891 | 20 | 85.9 | 3.520 9311 | 18 | 90.9 | 3.620 4301 | 16 | 95.9 | 3.715 9071 | 16 |
| 81.0 | 3.419 1145 | 19 | 86.0 | 3.522 9631 | 18 | 91.0 | 3.622 3778 | 17 | 96.0 | 3.717 7781 | 13 |
| 81.1 | 3.421 2380 | 20 | 86.1 | 3.524 9933 | 17 | 91.1 | 3.624 3238 | 15 | 96.1 | 3.719 6478 | 15 |
| 81.2 | 3.423 3595 | 20 | 86.2 | 3.527 0218 | 18 | 91.2 | 3.626 2683 | 17 | 96.2 | 3.721 5160 | 15 |
| 81.3 | 3.425 4790 | 19 | 86.3 | 3.529 0485 | 17 | 91.3 | 3.628 2111 | 15 | 96.3 | 3.723 3827 | 15 |
| 81.4 | 3.427 5966 | 19 | 86.4 | 3.531 0735 | 18 | 91.4 | 3.630 1524 | 16 | 96.4 | 3.725 2479 | 13 |
| 81.5 | 3.429 7123 | 20 | 86.5 | 3.533 0987 | 18 | 91.5 | 3.632 0921 | 17 | 96.5 | 3.727 1118 | 16 |
| 81.6 | 3.431 8260 | 20 | 86.6 | 3.535 1181 | 17 | 91.6 | 3.634 0301 | 15 | 96.6 | 3.728 9741 | 13 |
| 81.7 | 3.433 9377 | 19 | 86.7 | 3.537 1378 | 18 | 91.7 | 3.635 9666 | 15 | 96.7 | 3.730 8351 | 15 |
| 81.8 | 3.436 0475 | 19 | 86.8 | 3.539 1557 | 17 | 91.8 | 3.637 9016 | 17 | 96.8 | 3.732 6946 | 15 |
| 81.9 | 3.438 1564 | 19 | 86.9 | 3.541 1719 | 17 | 91.9 | 3.639 8349 | 16 | 96.9 | 3.734 5526 | 14 |
| 82.0 | 3.440 2614 | 20 | 87.0 | 3.543 1864 | 18 | 92.0 | 3.641 7666 | 15 | 97.0 | 3.736 4092 | 14 |
| 82.1 | 3.442 3664 | 19 | 87.1 | 3.545 1991 | 17 | 92.1 | 3.643 6968 | 16 | 97.1 | 3.738 2644 | 14 |
| 82.2 | 3.444 4675 | 19 | 87.2 | 3.547 2101 | 17 | 92.2 | 3.645 6254 | 15 | 97.2 | 3.740 1182 | 15 |
| 82.3 | 3.446 5677 | 19 | 87.3 | 3.549 2194 | 18 | 92.3 | 3.647 5525 | 16 | 97.3 | 3.741 9705 | 14 |
| 82.4 | 3.448 6660 | 20 | 87.4 | 3.551 2269 | 17 | 92.4 | 3.649 4780 | 16 | 97.4 | 3.743 8214 | 14 |
| 82.5 | 3.450 7623 | 18 | 87.5 | 3.553 2327 | 17 | 92.5 | 3.651 4019 | 15 | 97.5 | 3.745 6709 | 15 |
| 82.6 | 3.452 8568 | 19 | 87.6 | 3.555 2368 | 17 | 92.6 | 3.653 3243 | 16 | 97.6 | 3.747 5189 | 14 |
| 82.7 | 3.454 9494 | 20 | 87.7 | 3.557 2392 | 17 | 92.7 | 3.655 2451 | 16 | 97.7 | 3.749 3655 | 13 |
| 82.8 | 3.457 0400 | 18 | 87.8 | 3.559 2399 | 18 | 92.8 | 3.657 1643 | 15 | 97.8 | 3.751 2108 | 15 |
| 82.9 | 3.459 1288 | 19 | 87.9 | 3.561 2388 | 16 | 92.9 | 3.659 0820 | 15 | 97.9 | 3.753 0546 | 14 |
| 83.0 | 3.461 2157 | 19 | 88.0 | 3.563 2361 | 17 | 93.0 | 3.660 9982 | 16 | 98.0 | 3.754 8970 | 14 |
| 83.1 | 3.463 3007 | 19 | 88.1 | 3.565 2317 | 18 | 93.1 | 3.662 9128 | 15 | 98.1 | 3.756 7380 | 14 |
| 83.2 | 3.465 3838 | 19 | 88.2 | 3.567 2255 | 16 | 93.2 | 3.664 8259 | 16 | 98.2 | 3.758 5776 | 15 |
| 83.3 | 3.467 4650 | 18 | 88.3 | 3.569 2177 | 17 | 93.3 | 3.666 7374 | 15 | 98.3 | 3.760 4157 | 13 |
| 83.4 | 3.469 5444 | 19 | 88.4 | 3.571 2082 | 18 | 93.4 | 3.668 6474 | 15 | 98.4 | 3.762 2525 | 14 |
| 83.5 | 3.471 6219 | 19 | 88.5 | 3.573 1969 | 16 | 93.5 | 3.670 5559 | 15 | 98.5 | 3.764 0879 | 14 |
| 83.6 | 3.473 6975 | 18 | 88.6 | 3.575 1840 | 16 | 93.6 | 3.672 4629 | 16 | 98.6 | 3.765 9219 | 14 |
| 83.7 | 3.475 7713 | 19 | 88.7 | 3.577 1695 | 18 | 93.7 | 3.674 3683 | 15 | 98.7 | 3.767 7545 | 14 |
| 83.8 | 3.477 8432 | 18 | 88.8 | 3.579 1532 | 16 | 93.8 | 3.676 2722 | 16 | 98.8 | 3.769 5857 | 13 |
| 83.9 | 3.479 9133 | 19 | 88.9 | 3.581 1353 | 17 | 93.9 | 3.678 1745 | 14 | 98.9 | 3.771 4156 | 15 |
| 84.0 | 3.481 9815 | 19 | 89.0 | 3.583 1157 | 17 | 94.0 | 3.680 0754 | 16 | 99.0 | 3.773 2440 | 13 |
| 84.1 | 3.484 0478 | 17 | 89.1 | 3.585 0944 | 16 | 94.1 | 3.681 9747 | 14 | 99.1 | 3.775 0711 | 15 |
| 84.2 | 3.486 1124 | 20 | 89.2 | 3.587 0715 | 17 | 94.2 | 3.683 8726 | 16 | 99.2 | 3.776 8967 | 13 |
| 84.3 | 3.488 1750 | 17 | 89.3 | 3.589 0469 | 17 | 94.3 | 3.685 7689 | 15 | 99.3 | 3.778 7210 | 13 |
| 84.4 | 3.490 2359 | 19 | 89.4 | 3.591 0206 | 16 | 94.4 | 3.687 6637 | 15 | 99.4 | 3.780 5440 | 15 |
| 84.5 | 3.492 2949 | 18 | 89.5 | 3.592 9927 | 16 | 94.5 | 3.689 5570 | 15 | 99.5 | 3.782 3655 | 13 |
| 84.6 | 3.494 3521 | 18 | 89.6 | 3.594 9632 | 17 | 94.6 | 3.691 4488 | 15 | 99.6 | 3.784 1857 | 14 |
| 84.7 | 3.496 4075 | 19 | 89.7 | 3.596 9320 | 17 | 94.7 | 3.693 3391 | 14 | 99.7 | 3.786 0045 | 13 |
| 84.8 | 3.498 4610 | 17 | 89.8 | 3.598 8991 | 16 | 94.8 | 3.695 2280 | 16 | 99.8 | 3.787 8220 | 14 |
| 84.9 | 3.500 5128 | 19 | 89.9 | 3.600 8646 | 16 | 94.9 | 3.697 1153 | 15 | 99.9 | 3.789 6381 | 14 |
| 85.0 | 3.502 5627 | 18 | 90.0 | 3.602 8285 | 17 | 95.0 | 3.699 0011 | 14 | 100.0 | 3.791 4528 | 14 |

TABLE I.

| D | μ | δ^a | D | μ | δ^a | D | μ | δ^a | D | μ | δ^a |
|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|
| 100 | 3.791 463 | 136 | 150 | 4.566 193 | 66 | 200 | 5.167 521 | 39 | 250 | 5.667 009 | 28 |
| 101 | 3.809 526 | 134 | 151 | 4.579 574 | 65 | 201 | 5.178 358 | 39 | 251 | 5.676 225 | 26 |
| 102 | 3.827 465 | 130 | 152 | 4.592 890 | 66 | 202 | 5.189 156 | 40 | 252 | 5.685 415 | 27 |
| 103 | 3.845 274 | 130 | 153 | 4.606 140 | 63 | 203 | 5.199 914 | 38 | 253 | 5.694 578 | 25 |
| 104 | 3.862 953 | 126 | 154 | 4.619 327 | 63 | 204 | 5.210 634 | 38 | 254 | 5.703 716 | 27 |
| 105 | 3.880 506 | 125 | 155 | 4.632 451 | 62 | 205 | 5.221 316 | 39 | 255 | 5.712 827 | 25 |
| 106 | 3.897 934 | 122 | 156 | 4.645 513 | 62 | 206 | 5.231 959 | 37 | 256 | 5.721 913 | 26 |
| 107 | 3.915 240 | 121 | 157 | 4.658 513 | 61 | 207 | 5.242 565 | 37 | 257 | 5.730 973 | 26 |
| 108 | 3.932 425 | 118 | 158 | 4.671 452 | 61 | 208 | 5.253 134 | 38 | 258 | 5.740 007 | 25 |
| 109 | 3.949 492 | 117 | 159 | 4.684 330 | 59 | 209 | 5.263 665 | 36 | 259 | 5.749 016 | 25 |
| 110 | 3.966 442 | 115 | 160 | 4.697 149 | 59 | 210 | 5.274 160 | 36 | 260 | 5.758 000 | 25 |
| 111 | 3.983 277 | 112 | 161 | 4.709 909 | 58 | 211 | 5.284 619 | 37 | 261 | 5.766 959 | 24 |
| 112 | 4.000 000 | 112 | 162 | 4.722 611 | 58 | 212 | 5.295 041 | 35 | 262 | 5.775 894 | 26 |
| 113 | 4.016 611 | 109 | 163 | 4.735 255 | 57 | 213 | 5.305 428 | 36 | 263 | 5.784 803 | 23 |
| 114 | 4.033 113 | 107 | 164 | 4.747 842 | 56 | 214 | 5.315 779 | 35 | 264 | 5.793 689 | 26 |
| 115 | 4.049 508 | 107 | 165 | 4.760 373 | 56 | 215 | 5.326 095 | 35 | 265 | 5.802 549 | 23 |
| 116 | 4.065 796 | 104 | 166 | 4.772 848 | 56 | 216 | 5.336 376 | 35 | 266 | 5.811 386 | 24 |
| 117 | 4.081 980 | 103 | 167 | 4.785 267 | 54 | 217 | 5.346 622 | 34 | 267 | 5.820 199 | 24 |
| 118 | 4.098 061 | 101 | 168 | 4.797 632 | 54 | 218 | 5.356 834 | 33 | 268 | 5.828 988 | 23 |
| 119 | 4.114 041 | 100 | 169 | 4.809 943 | 54 | 219 | 5.367 013 | 35 | 269 | 5.837 754 | 24 |
| 120 | 4.129 921 | 98 | 170 | 4.822 200 | 52 | 220 | 5.377 157 | 33 | 270 | 5.846 496 | 24 |
| 121 | 4.145 703 | 98 | 171 | 4.834 405 | 53 | 221 | 5.387 268 | 34 | 271 | 5.855 214 | 22 |
| 122 | 4.161 387 | 94 | 172 | 4.846 557 | 52 | 222 | 5.397 345 | 32 | 272 | 5.863 910 | 24 |
| 123 | 4.176 977 | 95 | 173 | 4.858 657 | 51 | 223 | 5.407 390 | 34 | 273 | 5.872 582 | 23 |
| 124 | 4.192 472 | 92 | 174 | 4.870 706 | 51 | 224 | 5.417 401 | 31 | 274 | 5.881 231 | 22 |
| 125 | 4.207 875 | 92 | 175 | 4.882 704 | 50 | 225 | 5.427 381 | 33 | 275 | 5.889 858 | 23 |
| 126 | 4.223 186 | 90 | 176 | 4.894 652 | 50 | 226 | 5.437 328 | 32 | 276 | 5.898 462 | 22 |
| 127 | 4.238 407 | 89 | 177 | 4.906 550 | 50 | 227 | 5.447 243 | 31 | 277 | 5.907 044 | 23 |
| 128 | 4.253 539 | 88 | 178 | 4.918 398 | 48 | 228 | 5.457 127 | 32 | 278 | 5.915 603 | 22 |
| 129 | 4.268 583 | 86 | 179 | 4.930 198 | 48 | 229 | 5.466 979 | 32 | 279 | 5.924 140 | 21 |
| 130 | 4.283 541 | 85 | 180 | 4.941 950 | 48 | 230 | 5.476 799 | 30 | 280 | 5.932 656 | 23 |
| 131 | 4.298 414 | 85 | 181 | 4.953 654 | 48 | 231 | 5.486 589 | 31 | 281 | 5.941 149 | 22 |
| 132 | 4.313 202 | 82 | 182 | 4.965 310 | 46 | 232 | 5.496 348 | 30 | 282 | 5.949 620 | 21 |
| 133 | 4.327 908 | 83 | 183 | 4.976 920 | 47 | 233 | 5.506 077 | 31 | 283 | 5.958 070 | 21 |
| 134 | 4.342 531 | 80 | 184 | 4.988 483 | 46 | 234 | 5.515 775 | 30 | 284 | 5.966 499 | 22 |
| 135 | 4.357 074 | 80 | 185 | 5.000 000 | 45 | 235 | 5.525 443 | 29 | 285 | 5.974 906 | 21 |
| 136 | 4.371 537 | 78 | 186 | 5.011 472 | 46 | 236 | 5.535 082 | 30 | 286 | 5.983 292 | 22 |
| 137 | 4.385 922 | 79 | 187 | 5.022 898 | 44 | 237 | 5.544 691 | 30 | 287 | 5.991 656 | 20 |
| 138 | 4.400 228 | 76 | 188 | 5.034 280 | 45 | 238 | 5.554 270 | 29 | 288 | 6.000 000 | 21 |
| 139 | 4.414 458 | 75 | 189 | 5.045 617 | 43 | 239 | 5.563 820 | 28 | 289 | 6.008 323 | 21 |
| 140 | 4.428 613 | 76 | 190 | 5.056 911 | 44 | 240 | 5.573 342 | 30 | 290 | 6.016 625 | 20 |
| 141 | 4.442 692 | 73 | 191 | 5.068 161 | 43 | 241 | 5.582 834 | 28 | 291 | 6.024 907 | 21 |
| 142 | 4.456 698 | 73 | 192 | 5.079 368 | 43 | 242 | 5.592 298 | 28 | 292 | 6.033 168 | 20 |
| 143 | 4.470 631 | 72 | 193 | 5.090 532 | 41 | 243 | 5.601 734 | 28 | 293 | 6.041 409 | 20 |
| 144 | 4.484 492 | 72 | 194 | 5.101 655 | 43 | 244 | 5.611 142 | 29 | 294 | 6.049 630 | 21 |
| 145 | 4.498 281 | 69 | 195 | 5.112 735 | 41 | 245 | 5.620 521 | 26 | 295 | 6.057 830 | 19 |
| 146 | 4.512 001 | 70 | 196 | 5.123 774 | 42 | 246 | 5.629 874 | 29 | 296 | 6.066 011 | 21 |
| 147 | 4.525 651 | 69 | 197 | 5.134 771 | 40 | 247 | 5.639 198 | 27 | 297 | 6.074 171 | 19 |
| 148 | 4.539 232 | 67 | 198 | 5.145 728 | 40 | 248 | 5.648 495 | 27 | 298 | 6.082 312 | 19 |
| 149 | 4.552 746 | 67 | 199 | 5.156 645 | 41 | 249 | 5.657 765 | 26 | 299 | 6.090 434 | 20 |
| 150 | 4.566 193 | 66 | 200 | 5.167 521 | 39 | 250 | 5.667 009 | 28 | 300 | 6.098 536 | 20 |

TABLE 1.

| D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 | D | μ | δ^2 |
|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|
| 300 | 6.098 536 | 20 | 350 | 6.481 031 | 16 | 400 | 6.826 234 | 12 | 450 | 7.141 974 | 10 |
| 301 | 6.106 618 | 19 | 351 | 6.488 269 | 14 | 401 | 6.832 816 | 12 | 451 | 7.148 029 | 10 |
| 302 | 6.114 681 | 19 | 352 | 6.495 493 | 15 | 402 | 6.839 386 | 11 | 452 | 7.154 074 | 9 |
| 303 | 6.122 725 | 19 | 353 | 6.502 702 | 15 | 403 | 6.845 945 | 12 | 453 | 7.160 110 | 9 |
| 304 | 6.130 750 | 19 | 354 | 6.509 896 | 14 | 404 | 6.852 492 | 11 | 454 | 7.166 137 | 10 |
| 305 | 6.138 756 | 18 | 355 | 6.517 076 | 14 | 405 | 6.859 028 | 12 | 455 | 7.172 154 | 9 |
| 306 | 6.146 744 | 20 | 356 | 6.524 242 | 15 | 406 | 6.865 552 | 11 | 456 | 7.178 162 | 9 |
| 307 | 6.154 712 | 18 | 357 | 6.531 393 | 14 | 407 | 6.872 065 | 11 | 457 | 7.184 161 | 10 |
| 308 | 6.162 662 | 19 | 358 | 6.538 530 | 15 | 408 | 6.878 567 | 12 | 458 | 7.190 150 | 9 |
| 309 | 6.170 593 | 18 | 359 | 6.545 652 | 13 | 409 | 6.885 057 | 11 | 459 | 7.196 130 | 9 |
| 310 | 6.178 506 | 18 | 360 | 6.552 761 | 15 | 410 | 6.891 536 | 11 | 460 | 7.202 101 | 10 |
| 311 | 6.186 401 | 19 | 361 | 6.559 855 | 13 | 411 | 6.898 004 | 12 | 461 | 7.208 062 | 8 |
| 312 | 6.194 277 | 17 | 362 | 6.566 936 | 15 | 412 | 6.904 460 | 10 | 462 | 7.214 015 | 10 |
| 313 | 6.202 136 | 19 | 363 | 6.574 002 | 13 | 413 | 6.910 906 | 12 | 463 | 7.219 958 | 9 |
| 314 | 6.209 976 | 18 | 364 | 6.581 055 | 14 | 414 | 6.917 340 | 11 | 464 | 7.225 892 | 8 |
| 315 | 6.217 798 | 17 | 365 | 6.588 094 | 14 | 415 | 6.923 763 | 10 | 465 | 7.231 818 | 10 |
| 316 | 6.225 603 | 18 | 366 | 6.595 119 | 14 | 416 | 6.930 176 | 12 | 466 | 7.237 734 | 9 |
| 317 | 6.233 390 | 18 | 367 | 6.602 130 | 13 | 417 | 6.936 577 | 10 | 467 | 7.243 641 | 8 |
| 318 | 6.241 159 | 17 | 368 | 6.609 128 | 14 | 418 | 6.942 968 | 12 | 468 | 7.249 540 | 10 |
| 319 | 6.248 911 | 17 | 369 | 6.616 112 | 13 | 419 | 6.949 347 | 10 | 469 | 7.255 429 | 8 |
| 320 | 6.256 646 | 18 | 370 | 6.623 083 | 14 | 420 | 6.955 716 | 10 | 470 | 7.261 310 | 10 |
| 321 | 6.264 363 | 17 | 371 | 6.630 040 | 13 | 421 | 6.962 075 | 12 | 471 | 7.267 181 | 8 |
| 322 | 6.272 063 | 17 | 372 | 6.636 984 | 13 | 422 | 6.968 422 | 10 | 472 | 7.273 044 | 9 |
| 323 | 6.279 746 | 18 | 373 | 6.643 915 | 14 | 423 | 6.974 759 | 11 | 473 | 7.278 898 | 8 |
| 324 | 6.287 411 | 16 | 374 | 6.650 832 | 13 | 424 | 6.981 085 | 11 | 474 | 7.284 744 | 10 |
| 325 | 6.295 060 | 17 | 375 | 6.657 736 | 13 | 425 | 6.987 400 | 10 | 475 | 7.290 580 | 8 |
| 326 | 6.302 692 | 17 | 376 | 6.664 627 | 13 | 426 | 6.993 705 | 10 | 476 | 7.296 408 | 8 |
| 327 | 6.310 307 | 16 | 377 | 6.671 505 | 12 | 427 | 7.000 000 | 11 | 477 | 7.302 228 | 9 |
| 328 | 6.317 906 | 17 | 378 | 6.678 371 | 14 | 428 | 7.006 284 | 10 | 478 | 7.308 039 | 9 |
| 329 | 6.325 488 | 17 | 379 | 6.685 223 | 13 | 429 | 7.012 558 | 11 | 479 | 7.313 841 | 9 |
| 330 | 6.333 053 | 15 | 380 | 6.692 062 | 13 | 430 | 7.018 821 | 10 | 480 | 7.319 634 | 8 |
| 331 | 6.340 603 | 18 | 381 | 6.698 888 | 12 | 431 | 7.025 074 | 10 | 481 | 7.325 419 | 8 |
| 332 | 6.348 135 | 15 | 382 | 6.705 702 | 13 | 432 | 7.031 317 | 11 | 482 | 7.331 196 | 9 |
| 333 | 6.355 652 | 17 | 383 | 6.712 503 | 12 | 433 | 7.037 549 | 9 | 483 | 7.336 964 | 8 |
| 334 | 6.363 152 | 15 | 384 | 6.719 292 | 13 | 434 | 7.043 772 | 11 | 484 | 7.342 724 | 9 |
| 335 | 6.370 637 | 17 | 385 | 6.726 068 | 13 | 435 | 7.049 984 | 10 | 485 | 7.348 475 | 8 |
| 336 | 6.378 105 | 15 | 386 | 6.732 831 | 12 | 436 | 7.056 186 | 10 | 486 | 7.354 218 | 8 |
| 337 | 6.385 558 | 17 | 387 | 6.739 582 | 13 | 437 | 7.062 378 | 10 | 487 | 7.359 953 | 9 |
| 338 | 6.392 994 | 15 | 388 | 6.746 320 | 12 | 438 | 7.068 560 | 11 | 488 | 7.365 679 | 8 |
| 339 | 6.400 415 | 16 | 389 | 6.753 046 | 12 | 439 | 7.074 731 | 9 | 489 | 7.371 397 | 8 |
| 340 | 6.407 820 | 15 | 390 | 6.759 760 | 12 | 440 | 7.080 893 | 10 | 490 | 7.377 107 | 9 |
| 341 | 6.415 210 | 16 | 391 | 6.766 462 | 13 | 441 | 7.087 045 | 9 | 491 | 7.382 808 | 7 |
| 342 | 6.422 584 | 15 | 392 | 6.773 151 | 12 | 442 | 7.093 188 | 11 | 492 | 7.388 502 | 9 |
| 343 | 6.429 943 | 15 | 393 | 6.779 828 | 12 | 443 | 7.099 320 | 10 | 493 | 7.394 187 | 8 |
| 344 | 6.437 287 | 16 | 394 | 6.786 493 | 11 | 444 | 7.105 442 | 9 | 494 | 7.399 864 | 8 |
| 345 | 6.444 615 | 15 | 395 | 6.793 147 | 13 | 445 | 7.111 555 | 10 | 495 | 7.405 533 | 8 |
| 346 | 6.451 928 | 15 | 396 | 6.799 788 | 12 | 446 | 7.117 658 | 9 | 496 | 7.411 194 | 9 |
| 347 | 6.459 226 | 15 | 397 | 6.806 417 | 12 | 447 | 7.123 752 | 11 | 497 | 7.416 846 | 7 |
| 348 | 6.466 509 | 15 | 398 | 6.813 034 | 11 | 448 | 7.129 835 | 9 | 498 | 7.422 491 | 8 |
| 349 | 6.473 777 | 14 | 399 | 6.819 640 | 12 | 449 | 7.135 909 | 9 | 499 | 7.428 128 | 8 |
| 350 | 6.481 031 | 16 | 400 | 6.826 234 | 12 | 450 | 7.141 974 | 10 | 500 | 7.433 757 | 8 |

TABLE 1.

| D | μ | δ^a | D | μ | δ^a | D | μ | δ^a | D | μ | δ^a |
|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|-----|-----------|------------|
| 500 | 7.433 757 | 8 | 550 | 7.705 616 | 7 | 600 | 7.980 802 | 6 | 650 | 8.201 085 | 4 |
| 501 | 7.439 378 | 8 | 551 | 7.710 872 | 6 | 601 | 7.985 547 | 6 | 651 | 8.205 761 | 6 |
| 502 | 7.444 991 | 8 | 552 | 7.716 122 | 8 | 602 | 7.970 486 | 6 | 652 | 8.210 431 | 5 |
| 503 | 7.450 596 | 8 | 553 | 7.721 364 | 6 | 603 | 7.975 419 | 5 | 653 | 8.215 096 | 4 |
| 504 | 7.456 193 | 7 | 554 | 7.726 600 | 6 | 604 | 7.980 347 | 6 | 654 | 8.219 757 | 6 |
| 505 | 7.461 783 | 9 | 555 | 7.731 830 | 7 | 605 | 7.985 269 | 6 | 655 | 8.224 412 | 5 |
| 506 | 7.467 364 | 7 | 556 | 7.737 053 | 7 | 606 | 7.990 185 | 6 | 656 | 8.229 082 | 4 |
| 507 | 7.472 938 | 8 | 557 | 7.742 289 | 6 | 607 | 7.995 095 | 5 | 657 | 8.233 708 | 6 |
| 508 | 7.478 504 | 8 | 558 | 7.747 479 | 7 | 608 | 8.000 000 | 6 | 658 | 8.238 348 | 4 |
| 509 | 7.484 062 | 7 | 559 | 7.752 682 | 6 | 609 | 8.004 899 | 5 | 659 | 8.242 984 | 6 |
| 510 | 7.489 613 | 8 | 560 | 7.757 879 | 7 | 610 | 8.009 793 | 6 | 660 | 8.247 614 | 4 |
| 511 | 7.495 156 | 7 | 561 | 7.763 069 | 7 | 611 | 8.014 681 | 6 | 661 | 8.252 240 | 5 |
| 512 | 7.500 692 | 9 | 562 | 7.768 252 | 6 | 612 | 8.019 563 | 6 | 662 | 8.256 861 | 5 |
| 513 | 7.506 219 | 7 | 563 | 7.773 429 | 6 | 613 | 8.024 439 | 4 | 663 | 8.261 477 | 5 |
| 514 | 7.511 739 | 7 | 564 | 7.778 600 | 7 | 614 | 8.029 311 | 7 | 664 | 8.266 088 | 5 |
| 515 | 7.517 252 | 8 | 565 | 7.783 764 | 6 | 615 | 8.034 176 | 5 | 665 | 8.270 694 | 5 |
| 516 | 7.522 757 | 7 | 566 | 7.788 922 | 6 | 616 | 8.039 036 | 5 | 666 | 8.275 295 | 4 |
| 517 | 7.528 255 | 8 | 567 | 7.794 074 | 7 | 617 | 8.043 891 | 6 | 667 | 8.279 892 | 5 |
| 518 | 7.533 745 | 8 | 568 | 7.799 219 | 7 | 618 | 8.048 740 | 6 | 668 | 8.284 484 | 6 |
| 519 | 7.539 227 | 7 | 569 | 7.804 357 | 6 | 619 | 8.053 583 | 5 | 669 | 8.289 070 | 3 |
| 520 | 7.544 702 | 7 | 570 | 7.809 489 | 6 | 620 | 8.058 421 | 5 | 670 | 8.293 653 | 6 |
| 521 | 7.550 170 | 8 | 571 | 7.814 616 | 6 | 621 | 8.063 254 | 6 | 671 | 8.298 230 | 5 |
| 522 | 7.555 630 | 7 | 572 | 7.819 735 | 6 | 622 | 8.068 081 | 6 | 672 | 8.302 802 | 4 |
| 523 | 7.561 083 | 7 | 573 | 7.824 849 | 7 | 623 | 8.072 902 | 5 | 673 | 8.307 370 | 5 |
| 524 | 7.566 529 | 8 | 574 | 7.829 956 | 6 | 624 | 8.077 718 | 5 | 674 | 8.311 933 | 4 |
| 525 | 7.571 967 | 7 | 575 | 7.835 057 | 7 | 625 | 8.082 529 | 5 | 675 | 8.316 492 | 6 |
| 526 | 7.577 398 | 7 | 576 | 7.840 151 | 5 | 626 | 8.087 335 | 6 | 676 | 8.321 045 | 4 |
| 527 | 7.582 822 | 7 | 577 | 7.845 240 | 7 | 627 | 8.092 135 | 6 | 677 | 8.325 594 | 5 |
| 528 | 7.588 239 | 8 | 578 | 7.850 322 | 6 | 628 | 8.096 929 | 4 | 678 | 8.330 138 | 4 |
| 529 | 7.593 648 | 7 | 579 | 7.855 398 | 6 | 629 | 8.101 719 | 6 | 679 | 8.334 678 | 5 |
| 530 | 7.599 050 | 7 | 580 | 7.860 468 | 6 | 630 | 8.106 503 | 6 | 680 | 8.339 213 | 5 |
| 531 | 7.604 445 | 7 | 581 | 7.865 532 | 7 | 631 | 8.111 281 | 4 | 681 | 8.343 743 | 4 |
| 532 | 7.609 833 | 8 | 582 | 7.870 589 | 5 | 632 | 8.116 055 | 6 | 682 | 8.348 269 | 6 |
| 533 | 7.615 213 | 6 | 583 | 7.875 641 | 7 | 633 | 8.120 823 | 5 | 683 | 8.352 789 | 3 |
| 534 | 7.620 587 | 8 | 584 | 7.880 686 | 5 | 634 | 8.125 586 | 6 | 684 | 8.357 306 | 6 |
| 535 | 7.625 953 | 6 | 585 | 7.885 726 | 7 | 635 | 8.130 343 | 4 | 685 | 8.361 817 | 4 |
| 536 | 7.631 313 | 8 | 586 | 7.890 759 | 5 | 636 | 8.135 096 | 6 | 686 | 8.366 324 | 4 |
| 537 | 7.636 665 | 7 | 587 | 7.895 787 | 7 | 637 | 8.139 843 | 5 | 687 | 8.370 827 | 5 |
| 538 | 7.642 010 | 6 | 588 | 7.900 808 | 6 | 638 | 8.144 585 | 6 | 688 | 8.375 325 | 5 |
| 539 | 7.647 349 | 8 | 589 | 7.905 823 | 5 | 639 | 8.149 321 | 4 | 689 | 8.379 818 | 4 |
| 540 | 7.652 680 | 6 | 590 | 7.910 833 | 7 | 640 | 8.154 053 | 6 | 690 | 8.384 307 | 5 |
| 541 | 7.658 005 | 8 | 591 | 7.915 836 | 5 | 641 | 8.158 779 | 5 | 691 | 8.388 791 | 4 |
| 542 | 7.663 322 | 6 | 592 | 7.920 834 | 7 | 642 | 8.163 500 | 5 | 692 | 8.393 271 | 5 |
| 543 | 7.668 633 | 7 | 593 | 7.925 825 | 5 | 643 | 8.168 216 | 5 | 693 | 8.397 746 | 4 |
| 544 | 7.673 937 | 8 | 594 | 7.930 811 | 6 | 644 | 8.172 927 | 5 | 694 | 8.402 217 | 5 |
| 545 | 7.679 233 | 6 | 595 | 7.935 791 | 6 | 645 | 8.177 633 | 5 | 695 | 8.406 683 | 4 |
| 546 | 7.684 523 | 6 | 596 | 7.940 765 | 6 | 646 | 8.182 334 | 6 | 696 | 8.411 145 | 5 |
| 547 | 7.689 807 | 8 | 597 | 7.945 733 | 6 | 647 | 8.187 029 | 4 | 697 | 8.415 602 | 4 |
| 548 | 7.695 083 | 6 | 598 | 7.950 695 | 6 | 648 | 8.191 720 | 6 | 698 | 8.420 055 | 5 |
| 549 | 7.700 353 | 7 | 599 | 7.955 651 | 5 | 649 | 8.196 405 | 5 | 699 | 8.424 503 | 4 |
| 550 | 7.705 616 | 7 | 600 | 7.960 602 | 6 | 650 | 8.201 085 | 4 | 700 | 8.428 947 | 5 |

TABLE 1.

| D | μ | D | μ | D | μ | D | μ |
|-----|---------------------------|-----|---------------------------|-----|---------------------------|-----|---------------------------|
| 700 | 8.428 947 ₄₄₃₉ | 750 | 8.645 707 ₄₂₃₁ | 800 | 8.852 614 ₄₀₄₆ | 850 | 9.050 708 ₃₈₇₈ |
| 701 | 8.433 386 ₄₄₃₅ | 751 | 8.649 938 ₄₂₂₇ | 801 | 8.856 660 ₄₀₄₁ | 851 | 9.054 586 ₃₈₇₅ |
| 702 | 8.437 821 ₄₄₃₁ | 752 | 8.654 165 ₄₂₂₃ | 802 | 8.860 701 ₄₀₃₈ | 852 | 9.058 461 ₃₈₇₂ |
| 703 | 8.442 252 ₄₄₂₆ | 753 | 8.658 388 ₄₂₁₉ | 803 | 8.864 739 ₄₀₃₅ | 853 | 9.062 335 ₃₈₆₈ |
| 704 | 8.446 678 ₄₄₂₂ | 754 | 8.662 607 ₄₂₁₆ | 804 | 8.868 774 ₄₀₃₁ | 854 | 9.066 201 ₃₈₆₆ |
| 705 | 8.451 100 ₄₄₁₈ | 755 | 8.666 823 ₄₂₁₁ | 805 | 8.872 805 ₄₀₂₇ | 855 | 9.070 067 ₃₈₆₃ |
| 706 | 8.455 518 ₄₄₁₃ | 756 | 8.671 034 ₄₂₀₈ | 806 | 8.876 832 ₄₀₂₅ | 856 | 9.073 930 ₃₈₅₉ |
| 707 | 8.459 931 ₄₄₀₈ | 757 | 8.675 242 ₄₂₀₃ | 807 | 8.880 857 ₄₀₂₀ | 857 | 9.077 789 ₃₈₅₆ |
| 708 | 8.464 339 ₄₄₀₅ | 758 | 8.679 445 ₄₂₀₀ | 808 | 8.884 877 ₄₀₁₇ | 858 | 9.081 645 ₃₈₅₃ |
| 709 | 8.468 744 ₄₄₀₀ | 759 | 8.683 645 ₄₁₉₆ | 809 | 8.888 894 ₄₀₁₄ | 859 | 9.085 498 ₃₈₅₀ |
| 710 | 8.473 144 ₄₃₉₅ | 760 | 8.687 841 ₄₁₉₂ | 810 | 8.892 908 ₄₀₁₀ | 860 | 9.089 348 ₃₈₄₇ |
| 711 | 8.477 539 ₄₃₉₂ | 761 | 8.692 033 ₄₁₈₈ | 811 | 8.896 918 ₄₀₀₇ | 861 | 9.093 195 ₃₈₄₄ |
| 712 | 8.481 931 ₄₃₈₇ | 762 | 8.696 221 ₄₁₈₅ | 812 | 8.900 925 ₄₀₀₄ | 862 | 9.097 039 ₃₈₄₀ |
| 713 | 8.486 318 ₄₃₈₃ | 763 | 8.700 406 ₄₁₈₀ | 813 | 8.904 929 ₄₀₀₀ | 863 | 9.100 879 ₃₈₃₈ |
| 714 | 8.490 701 ₄₃₇₈ | 764 | 8.704 586 ₄₁₇₇ | 814 | 8.908 929 ₃₉₉₆ | 864 | 9.104 717 ₃₈₃₄ |
| 715 | 8.495 079 ₄₃₇₅ | 765 | 8.708 763 ₄₁₇₃ | 815 | 8.912 925 ₃₉₉₃ | 865 | 9.108 551 ₃₈₃₂ |
| 716 | 8.499 454 ₄₃₇₀ | 766 | 8.712 936 ₄₁₆₉ | 816 | 8.916 918 ₃₉₉₀ | 866 | 9.112 383 ₃₈₂₈ |
| 717 | 8.503 824 ₄₃₆₅ | 767 | 8.717 105 ₄₁₆₆ | 817 | 8.920 908 ₃₉₈₇ | 867 | 9.116 211 ₃₈₂₅ |
| 718 | 8.508 189 ₄₃₆₂ | 768 | 8.721 271 ₄₁₆₁ | 818 | 8.924 895 ₃₉₈₃ | 868 | 9.120 036 ₃₈₂₂ |
| 719 | 8.512 551 ₄₃₅₇ | 769 | 8.725 432 ₄₁₅₈ | 819 | 8.928 878 ₃₉₇₉ | 869 | 9.123 858 ₃₈₂₀ |
| 720 | 8.516 908 ₄₃₅₃ | 770 | 8.729 590 ₄₁₅₄ | 820 | 8.932 857 ₃₉₇₆ | 870 | 9.127 678 ₃₈₁₆ |
| 721 | 8.521 261 ₄₃₄₉ | 771 | 8.733 744 ₄₁₅₁ | 821 | 8.936 833 ₃₉₇₃ | 871 | 9.131 494 ₃₈₁₃ |
| 722 | 8.525 610 ₄₃₄₄ | 772 | 8.737 895 ₄₁₄₆ | 822 | 8.940 806 ₃₉₇₀ | 872 | 9.135 307 ₃₈₁₀ |
| 723 | 8.529 954 ₄₃₄₁ | 773 | 8.742 041 ₄₁₄₃ | 823 | 8.944 776 ₃₉₆₆ | 873 | 9.139 117 ₃₈₀₇ |
| 724 | 8.534 295 ₄₃₃₆ | 774 | 8.746 184 ₄₁₃₉ | 824 | 8.948 742 ₃₉₆₃ | 874 | 9.142 924 ₃₈₀₄ |
| 725 | 8.538 631 ₄₃₃₂ | 775 | 8.750 323 ₄₁₃₆ | 825 | 8.952 705 ₃₉₅₉ | 875 | 9.146 728 ₃₈₀₁ |
| 726 | 8.542 963 ₄₃₂₈ | 776 | 8.754 459 ₄₁₃₁ | 826 | 8.956 664 ₃₉₅₆ | 876 | 9.150 529 ₃₇₉₈ |
| 727 | 8.547 291 ₄₃₂₄ | 777 | 8.758 590 ₄₁₂₈ | 827 | 8.960 620 ₃₉₅₃ | 877 | 9.154 327 ₃₇₉₅ |
| 728 | 8.551 615 ₄₃₂₀ | 778 | 8.762 718 ₄₁₂₅ | 828 | 8.964 573 ₃₉₅₀ | 878 | 9.158 122 ₃₇₉₁ |
| 729 | 8.555 935 ₄₃₁₆ | 779 | 8.766 843 ₄₁₂₀ | 829 | 8.968 523 ₃₉₄₆ | 879 | 9.161 913 ₃₇₈₉ |
| 730 | 8.560 250 ₄₃₁₂ | 780 | 8.770 963 ₄₁₁₇ | 830 | 8.972 469 ₃₉₄₃ | 880 | 9.165 702 ₃₇₈₆ |
| 731 | 8.564 562 ₄₃₀₇ | 781 | 8.775 080 ₄₁₁₄ | 831 | 8.976 412 ₃₉₃₉ | 881 | 9.169 488 ₃₇₈₃ |
| 732 | 8.568 869 ₄₃₀₃ | 782 | 8.779 194 ₄₁₀₉ | 832 | 8.980 351 ₃₉₃₇ | 882 | 9.173 271 ₃₇₈₀ |
| 733 | 8.573 172 ₄₂₉₉ | 783 | 8.783 303 ₄₁₀₆ | 833 | 8.984 288 ₃₉₃₃ | 883 | 9.177 051 ₃₇₇₇ |
| 734 | 8.577 471 ₄₂₉₅ | 784 | 8.787 409 ₄₁₀₃ | 834 | 8.988 221 ₃₉₂₉ | 884 | 9.180 828 ₃₇₇₄ |
| 735 | 8.581 766 ₄₂₉₁ | 785 | 8.791 512 ₄₀₉₈ | 835 | 8.992 150 ₃₉₂₇ | 885 | 9.184 602 ₃₇₇₁ |
| 736 | 8.586 057 ₄₂₈₇ | 786 | 8.795 610 ₄₀₉₅ | 836 | 8.996 077 ₃₉₂₃ | 886 | 9.188 373 ₃₇₆₉ |
| 737 | 8.590 344 ₄₂₈₃ | 787 | 8.799 708 ₄₀₉₂ | 837 | 9.000 000 ₃₉₂₀ | 887 | 9.192 142 ₃₇₆₅ |
| 738 | 8.594 627 ₄₂₇₈ | 788 | 8.803 797 ₄₀₈₈ | 838 | 9.003 920 ₃₉₁₇ | 888 | 9.195 907 ₃₇₆₂ |
| 739 | 8.598 905 ₄₂₇₅ | 789 | 8.807 885 ₄₀₈₄ | 839 | 9.007 837 ₃₉₁₃ | 889 | 9.199 669 ₃₇₅₉ |
| 740 | 8.603 180 ₄₂₇₁ | 790 | 8.811 969 ₄₀₈₀ | 840 | 9.011 750 ₃₉₁₀ | 890 | 9.203 428 ₃₇₅₇ |
| 741 | 8.607 451 ₄₂₆₆ | 791 | 8.816 045 ₄₀₇₇ | 841 | 9.015 660 ₃₉₀₇ | 891 | 9.207 185 ₃₇₅₃ |
| 742 | 8.611 717 ₄₂₆₃ | 792 | 8.820 126 ₄₀₇₄ | 842 | 9.019 567 ₃₉₀₄ | 892 | 9.210 938 ₃₇₅₁ |
| 743 | 8.615 980 ₄₂₅₉ | 793 | 8.824 200 ₄₀₇₀ | 843 | 9.023 471 ₃₉₀₁ | 893 | 9.214 689 ₃₇₄₇ |
| 744 | 8.620 239 ₄₂₅₄ | 794 | 8.828 276 ₄₀₆₆ | 844 | 9.027 372 ₃₈₉₇ | 894 | 9.218 436 ₃₇₄₅ |
| 745 | 8.624 493 ₄₂₅₁ | 795 | 8.832 336 ₄₀₆₃ | 845 | 9.031 269 ₃₈₉₄ | 895 | 9.222 181 ₃₇₄₂ |
| 746 | 8.628 744 ₄₂₄₇ | 796 | 8.836 399 ₄₀₅₉ | 846 | 9.035 163 ₃₈₉₁ | 896 | 9.225 923 ₃₇₃₉ |
| 747 | 8.632 991 ₄₂₄₃ | 797 | 8.840 458 ₄₀₅₆ | 847 | 9.039 054 ₃₈₈₈ | 897 | 9.229 662 ₃₇₃₆ |
| 748 | 8.637 234 ₄₂₃₈ | 798 | 8.844 514 ₄₀₅₂ | 848 | 9.042 942 ₃₈₈₄ | 898 | 9.233 398 ₃₇₃₃ |
| 749 | 8.641 472 ₄₂₃₅ | 799 | 8.848 566 ₄₀₄₈ | 849 | 9.046 826 ₃₈₈₂ | 899 | 9.237 131 ₃₇₃₀ |
| 750 | 8.645 707 | 800 | 8.852 614 | 850 | 9.050 708 | 900 | 9.240 861 |

TABLE 1.

TABLE 2.

| D | μ | D | μ |
|-----|---------------------------|------|---------------------------|
| 900 | 9.240 861 ₃₇₂₈ | 950 | 9.423 820 ₃₅₉₀ |
| 901 | 9.244 589 ₃₇₂₄ | 951 | 9.427 410 ₃₅₈₈ |
| 902 | 9.248 313 ₃₇₂₂ | 952 | 9.430 998 ₃₅₈₅ |
| 903 | 9.252 035 ₃₇₁₉ | 953 | 9.434 583 ₃₅₈₂ |
| 904 | 9.255 754 ₃₇₁₆ | 954 | 9.438 165 ₃₅₈₀ |
| 905 | 9.259 470 ₃₇₁₃ | 955 | 9.441 745 ₃₅₇₈ |
| 906 | 9.263 183 ₃₇₁₀ | 956 | 9.445 323 ₃₅₇₄ |
| 907 | 9.266 893 ₃₇₀₇ | 957 | 9.448 897 ₃₅₇₂ |
| 908 | 9.270 600 ₃₇₀₅ | 958 | 9.452 469 ₃₅₇₀ |
| 909 | 9.274 305 ₃₇₀₂ | 959 | 9.456 039 ₃₅₆₇ |
| 910 | 9.278 007 ₃₆₉₉ | 960 | 9.459 608 ₃₅₆₄ |
| 911 | 9.281 706 ₃₆₉₆ | 961 | 9.463 170 ₃₅₆₂ |
| 912 | 9.285 402 ₃₆₉₃ | 962 | 9.466 732 ₃₅₅₉ |
| 913 | 9.289 095 ₃₆₉₁ | 963 | 9.470 291 ₃₅₅₇ |
| 914 | 9.292 786 ₃₆₈₇ | 964 | 9.473 848 ₃₅₅₄ |
| 915 | 9.296 473 ₃₆₈₅ | 965 | 9.477 402 ₃₅₅₂ |
| 916 | 9.300 158 ₃₆₈₃ | 966 | 9.480 954 ₃₅₄₉ |
| 917 | 9.303 841 ₃₆₇₉ | 967 | 9.484 503 ₃₅₄₆ |
| 918 | 9.307 520 ₃₆₇₆ | 968 | 9.488 049 ₃₅₄₄ |
| 919 | 9.311 196 ₃₆₇₄ | 969 | 9.491 593 ₃₅₄₂ |
| 920 | 9.314 870 ₃₆₇₁ | 970 | 9.495 135 ₃₅₃₉ |
| 921 | 9.318 541 ₃₆₆₉ | 971 | 9.498 674 ₃₅₃₆ |
| 922 | 9.322 210 ₃₆₆₅ | 972 | 9.502 210 ₃₅₃₄ |
| 923 | 9.325 875 ₃₆₆₃ | 973 | 9.505 744 ₃₅₃₁ |
| 924 | 9.329 538 ₃₆₆₀ | 974 | 9.509 275 ₃₅₂₉ |
| 925 | 9.333 198 ₃₆₅₇ | 975 | 9.512 804 ₃₅₂₆ |
| 926 | 9.336 855 ₃₆₅₅ | 976 | 9.516 330 ₃₅₂₄ |
| 927 | 9.340 510 ₃₆₅₁ | 977 | 9.519 854 ₃₅₂₁ |
| 928 | 9.344 161 ₃₆₄₉ | 978 | 9.523 375 ₃₅₁₉ |
| 929 | 9.347 810 ₃₆₄₇ | 979 | 9.526 894 ₃₅₁₇ |
| 930 | 9.351 457 ₃₆₄₃ | 980 | 9.530 411 ₃₅₁₄ |
| 931 | 9.355 100 ₃₆₄₁ | 981 | 9.533 925 ₃₅₁₁ |
| 932 | 9.358 741 ₃₆₃₉ | 982 | 9.537 436 ₃₅₀₉ |
| 933 | 9.362 380 ₃₆₃₅ | 983 | 9.540 945 ₃₅₀₆ |
| 934 | 9.366 015 ₃₆₃₃ | 984 | 9.544 451 ₃₅₀₄ |
| 935 | 9.369 648 ₃₆₃₀ | 985 | 9.547 955 ₃₅₀₂ |
| 936 | 9.373 278 ₃₆₂₇ | 986 | 9.551 457 ₃₄₉₉ |
| 937 | 9.376 905 ₃₆₂₅ | 987 | 9.554 956 ₃₄₉₆ |
| 938 | 9.380 530 ₃₆₂₂ | 988 | 9.558 452 ₃₄₉₅ |
| 939 | 9.384 152 ₃₆₂₀ | 989 | 9.561 947 ₃₄₉₁ |
| 940 | 9.387 772 ₃₆₁₆ | 990 | 9.565 438 ₃₄₉₀ |
| 941 | 9.391 388 ₃₆₁₅ | 991 | 9.568 928 ₃₄₈₆ |
| 942 | 9.395 003 ₃₆₁₁ | 992 | 9.572 414 ₃₄₈₅ |
| 943 | 9.398 614 ₃₆₀₉ | 993 | 9.575 899 ₃₄₈₂ |
| 944 | 9.402 223 ₃₆₀₆ | 994 | 9.579 381 ₃₄₇₉ |
| 945 | 9.405 829 ₃₆₀₃ | 995 | 9.582 860 ₃₄₇₇ |
| 946 | 9.409 432 ₃₆₀₁ | 996 | 9.586 337 ₃₄₇₅ |
| 947 | 9.413 033 ₃₅₉₈ | 997 | 9.589 812 ₃₄₇₂ |
| 948 | 9.416 631 ₃₅₉₆ | 998 | 9.593 284 ₃₄₇₀ |
| 949 | 9.420 227 ₃₅₉₃ | 999 | 9.596 754 ₃₄₆₈ |
| 950 | 9.423 820 | 1000 | 9.600 222 |

| $4/D^{1/3}$ | R |
|-------------|--------------|
| 0.00 | 0.000 000 0 |
| .01 | 000 0 |
| .02 | 000 0 |
| .03 | 000 0 |
| .04 | 000 0 |
| 0.05 | 0.000 000 0 |
| .06 | 000 0 |
| .07 | 000 0 |
| .08 | 000 0 |
| .09 | 000 0 |
| 0.10 | 0.000 000 0 |
| .11 | 000 1 |
| .12 | 001 0 |
| .13 | 001 0 |
| .14 | 001 1 |
| 0.15 | 0.000 002 0 |
| .16 | 002 1 |
| .17 | 003 1 |
| .18 | 004 1 |
| .19 | 005 2 |
| 0.20 | 0.000 007 2 |
| .21 | 009 2 |
| .22 | 011 3 |
| .23 | 014 3 |
| .24 | 017 4 |
| 0.25 | 0.000 021 4 |
| .26 | 025 5 |
| .27 | 030 7 |
| .28 | 037 7 |
| .29 | 044 8 |
| 0.30 | 0.000 052 9 |
| .31 | 061 11 |
| .32 | 072 12 |
| .33 | 084 13 |
| .34 | 097 16 |
| 0.35 | 0.000 113 17 |
| .36 | 130 19 |
| .37 | 149 22 |
| .38 | 171 24 |
| .39 | 195 27 |
| 0.40 | 0.000 222 29 |
| .41 | 251 29 |

When $D > 1000$ use
 $\mu = D^{1/3} - 4/D^{1/3} + R$

as it is the one convenient in the other method suggested it was thought desirable to maintain uniformity.

Next is provided in Table 2 a convenient way of dealing with the problem when $D > 1,000$. Tartaglia's solution of the cubic equation gives

$$\begin{aligned}\mu &= \left\{ \frac{D}{2} + \frac{D}{2} \left(1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} + \left\{ \frac{D}{2} - \frac{D}{2} \left(1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} \\ &= D^{1/3} \left\{ \frac{1}{2} + \frac{1}{2} \left(1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} + D^{1/3} \left\{ \frac{1}{2} - \frac{1}{2} \left(1 + \frac{256}{D^2} \right)^{1/2} \right\}^{1/3} \\ &= D^{1/3} - \frac{4}{D^{1/3}} + \frac{2^6}{3} \frac{1}{D^{5/3}} + \frac{2^8}{3} \frac{1}{D^{7/3}} - \frac{2^{14}}{9} \frac{1}{D^{11/3}} - \frac{7 \cdot 2^{14}}{9} \frac{1}{D^{13/3}} + \dots,\end{aligned}$$

where the necessary binomial expansions are easily justified. Now place $4/D^{1/3} = d$ and write the solution

$$\mu = D^{1/3} - \frac{4}{D^{1/3}} + R,$$

$$\text{where } R = \frac{1}{2^4 \cdot 3} d^5 + \frac{1}{2^6 \cdot 3} d^7 - \frac{1}{2^8 \cdot 3^2} d^{11} - \frac{7}{2^{12} \cdot 3^2} d^{13} + \dots$$

Table 2 gives R with argument $4/D^{1/3}$ and the solution is performed for $D > 1000$ by obtaining $D^{1/3}$ by linear interpolation in Barlow's tables (Comrie, 1941), then calculating $4/D^{1/3}$ and finding R from the table. When $D > 12,500$, taking the computer beyond the table of cube roots in Barlow, one of the methods of finding cube roots explained in the introduction to that invaluable work may be used. The table was calculated from the series for R and the same remarks apply as for Table I except that no subtabulation was done, every value being computed.

For the computation of the other coordinate, λ , in the plane of the orbit μ^2 is needed. No table of μ^2 is given since it is quicker to calculate the square of a seven figure number with a machine than to interpolate for it from a table with argument D .

The constants of the equator are computed for the orbit from the formulae

$$\begin{aligned}A_x &= q \{ \cos \omega \cos \Omega - \sin \omega \sin \Omega \cos i \}, \\ B_x &= q \{ -\sin \omega \cos \Omega - \cos \omega \sin \Omega \cos i \}, \\ A_y &= q \{ (\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \cos \epsilon - \sin \omega \sin i \sin \epsilon \}, \\ B_y &= q \{ (\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \cos \epsilon - \cos \omega \sin i \sin \epsilon \}, \\ A_z &= q \{ \sin \omega \sin i \cos \epsilon + (\sin \omega \cos \Omega \cos i + \cos \omega \sin \Omega) \sin \epsilon \}, \\ B_z &= q \{ \cos \omega \sin i \cos \epsilon + (\cos \omega \cos \Omega \cos i - \sin \omega \sin \Omega) \sin \epsilon \},\end{aligned}$$

with the check formula

$$A_x B_x + A_y B_y + A_z B_z = 0.$$

Then having obtained μ in one of the above ways the rectangular equatorial heliocentric coordinates (x, y, z) may be calculated from

$$x = A_x - \frac{A_x}{4} \mu^2 + B_x \mu,$$

$$y = A_y - \frac{A_y}{4} \mu^2 + B_y \mu,$$

$$z = A_z - \frac{A_z}{4} \mu^2 + B_z \mu.$$

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RANK VARIATION IN VITRAIN AND RELATIONS TO THE PHYSICAL NATURE OF ITS CARBONISED PRODUCTS.

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INTRODUCTION.

The investigations recorded in this paper were carried out with the object of studying variations in the chemical properties of vitrains of all ranks, and also for the purpose of obtaining some fundamental data regarding general relationships between rank of vitrain and the physical nature of products of carbonisation under low-temperature conditions. Vitrain, the purest and most homogeneous of the petrological constituents in coal, was used to obtain comparable results and to avoid the influence of varying proportions of banded constituents which may obscure the significance of results obtained from seam-samples.

The present work on relation between rank of vitrain and physical nature of carbonisation products must be regarded as a preliminary reconnaissance in a wide field of problems where very little fundamental data is available. Carbonisation was carried out under one specific set of conditions, and results represent relationships for those conditions. The nature of cokes and chars depends on many factors such as temperature, rate of heating, pressure on the carbonising mass, and coarseness of the materials before heating. Variation in any of these factors may produce somewhat different results, and a great deal of research is required to elucidate all aspects of the problem. However, it is believed that results, recorded in this paper, have established some general relationships between degree of development of micelle structure in vitrain and the ultra-fine structure of its carbonisation products.

SELECTION AND PREPARATION OF MATERIAL.

Coals were selected to include as many members of the metamorphic series as possible, from immature peat to anthracite and graphite. The materials range in geological age from Carboniferous to Pleistocene. All important Australian coalfields are represented and materials are included from Great Britain, Germany, Canada, the United States and Antarctica. In the case of coals of sub-bituminous rank or lower, pieces of woody material were selected as the precursors of vitrain, and at the extreme low-rank end of the series a contemporary wood, *Eucalyptus corymbosa*, was included for comparative purposes. Where the coal was of higher rank, specimens containing well-developed vitrain bands were selected, and two or more individual bands, from 0.2 to 0.5 inch in thickness, were separated by hand from each specimen, or from several specimens from the same locality. In the graphitic coal from Rhode Island, U.S.A., the different petrological constituents could not be recognised, and although the coal was used to mark the high-rank extreme of the series, it must be regarded as a *whole coal* sample and not a true vitrain. Fifty-three different coals were selected to provide a complete range in rank. From these, vitrain was carefully separated by hand and granular samples were prepared by crushing, with the minimum production of fines, to pass

through a sieve with circular perforations of 0.06 inch diameter and to be retained on a sieve with perforations of 0.04 inch diameter. Vitrains of sub-bituminous rank or lower (i.e. 79% carbon or less) which undergo permanent moisture changes on drying, were maintained in their original water-saturated condition in all cases where maximum inherent moisture was to be determined. Sieved and graded vitrain from coals of sub-bituminous rank or higher were water-saturated then washed with dilute hydrochloric acid (5% solution) to remove adherent mineral matter, particularly carbonates, deposited in cleat planes. All traces of acid were then washed out, and after setting aside a few grammes of the water-saturated material for determination of maximum inherent moisture, the rest of the sample was air-dried.

METHODS OF ANALYSIS AND EXPERIMENTAL TECHNIQUE.

Ultimate and proximate analyses of all samples were carried out by standard technique, using apparatus with slight modifications but generally similar to that described by Himus (1946). Results of analyses are listed in Table 1. Carbon, hydrogen, volatiles and fixed carbon values are quoted on the ash-free, dry basis. Maximum inherent moistures of vitrains and their carbonised products were determined by controlled vaporisation of adherent moisture (Dulhunty, 1947) and results are quoted as percentages, representing grammes of moisture per 100 grammes of dry material. Throughout this paper, all moisture values and references to moisture represent *maximum inherent moisture* which is the total amount of moisture held in the material when all openings, small enough to lower the vapour pressure of water, are filled, and no adherent moisture of normal vapour pressure is present. As described earlier, vitrains separated from coals of sub-bituminous rank or lower were prepared and maintained in their original water-saturated condition to avoid irreversible changes which occur on air drying (Dulhunty, 1948); therefore, maximum inherent moisture values represent a true index of the physical rank of the materials.

A test was designed with the object of studying bulk-volume changes in granular samples of vitrain as a result of carbonisation under free-swelling, low-temperature conditions of heating.

Carbonisation was carried out in an iron tube with an inside diameter of 0.5 inch, and an overall length of 3.2 inches, closed at each end by ground iron plugs. One plug, at the top of the tube, was provided with a central hole of 0.125 inch diameter, for escape of volatiles. A 3.5 inches length of $\frac{7}{16}$ iron rod was used as a plunger, to measure the depths of vitrain filled into the tube and the residue after carbonisation. The tube, with the lower plug in position, was held vertically and granular vitrain added to a depth of approximately 1.02 inches, measured by inserting the plunger and resting it on the surface of the material which had previously been thoroughly settled down to constant level by gentle tapping. The tube was then heated with the plunger in position, at 110° C. for two hours in an atmosphere of nitrogen, to dry the vitrain. After heating, the plunger was removed and the tube, closed with a cork, was cooled in a stoppered test tube, and the depth of dry vitrain, approximately one inch in all cases, was measured. The plunger was then withdrawn, the upper iron plug inserted, the tube placed in a vertical tube-furnace and heated from room temperature to 600° C. under time-temperature conditions similar to those employed in the Gray King assay. The tube was then removed from the furnace and allowed to cool, after which the iron plug was removed and the depth of carbonised residue measured by inserting the plunger. The difference between measurements before and after carbonisation, representing expansion or contraction, was expressed as a percentage of the depth of dry vitrain originally contained in the tube. Low-temperature carbonisation of all members of the

TABLE I.
Properties of Hand Separated Vitrines.

| Spec. No. | Locality. | Geological Age. | Rank. | Per-centage Ash. | Ash-free, Dry Basis. | | | | | | Percentage Volume Change on Car-bonising. |
|-----------|-----------------------------|-----------------|----------------------|------------------|----------------------|------------------|-------------------|------------------|---------------------|----------------------|---|
| | | | | | At 925° C. | | At 600° C. | | Per-centage Carbon. | Percentage Hydrogen. | |
| | | | | | Per-centage Vols. | Per-centage F.C. | Per-centage Vols. | Per-centage F.C. | | | |
| 572 | Rhode Island, U.S.A. | Carb. | Graphite. | 14.1 | 3.8 | 96.2 | — | — | 97.3 | 2.0 | 0.0 |
| 622 | South Wales, Great Britain | Carb. | Anthrac. | 1.3 | 5.3 | 94.7 | — | — | 93.9 | 3.6 | -2.0 |
| 567 | Pennsylvania, U.S.A. | Carb. | Anthrac. | 4.0 | 5.7 | 94.3 | — | — | 93.0 | 3.7 | -1.1 |
| 497 | Largenbrahm, Ruhr, Germany. | Carb. | Anthrac. | 0.4 | 7.0 | 93.0 | — | — | 92.7 | 3.8 | -3.3 |
| 525 | Palmaise, Scotland | Carb. | Anthrac. | 1.9 | 6.1 | 93.9 | — | — | 92.3 | 3.5 | -4.5 |
| 208 | Baralaba, Queensland | Perm. | Semi-Anthrac. | 1.9 | 10.7 | 89.3 | 6.5 | 93.5 | 91.6 | 4.4 | -13.1 |
| 28 | Mittagong, N.S.W. | Perm. | Semi-Anthrac. | 5.7 | 7.4 | 92.6 | 3.5 | 96.5 | 91.5 | 3.3 | -11.1 |
| 161 | York Plains, Tasmania | Trias. | Semi-Anthrac. | 3.6 | 11.7 | 88.3 | 7.2 | 92.8 | 90.3 | 3.9 | -2.9 |
| 36 | Currabubula, N.S.W. | Perm. | High - rank Bitumin. | 22.0 | 15.7 | 84.3 | — | — | 89.2 | 4.2 | -7.1 |
| 310 | Aberdare, N.S.W. | Perm. | High - rank Bitumin. | 1.5 | 39.6 | 60.4 | 30.6 | 69.4 | 89.2 | 5.5 | +136.0 |
| 314 | Austinnmer, N.S.W. | Perm. | High - rank Bitumin. | 1.0 | 27.9 | 72.1 | — | — | 88.9 | 5.2 | +598.0 |
| 313 | Clifton, N.S.W. | Perm. | High - rank Bitumin. | 0.9 | 25.5 | 74.5 | 16.3 | 83.7 | 88.8 | 4.1 | +423.0 |
| 30 | Balmain, N.S.W. | Perm. | High - rank Bitumin. | 1.0 | 23.5 | 76.5 | 14.9 | 85.1 | 88.3 | 5.1 | +89.0 |
| 443 | Depto, N.S.W. | Perm. | High - rank Bitumin. | 2.5 | 29.0 | 71.0 | — | — | 88.1 | 5.3 | +496.0 |
| 312 | Helensburgh, N.S.W. | Perm. | High - rank Bitumin. | 0.8 | 24.9 | 75.1 | 17.8 | 82.2 | 88.0 | 4.7 | +476.7 |
| 644 | Undercliffe, N.S.W. | Trias. | High - rank Bitumin. | 0.7 | 36.1 | 63.9 | — | — | 85.3 | 4.9 | +524.0 |
| 347 | Berrima, N.S.W. | Perm. | High - rank Bitumin. | 3.5 | 33.3 | 66.7 | — | — | 84.8 | 5.4 | +99.1 |
| 348 | Sydney, N.S.W. | Trias. | High - rank Bitumin. | 0.8 | 36.3 | 63.7 | — | — | 84.2 | 5.1 | +298.9 |
| 646 | Catherine Hill Bay, N.S.W. | Perm. | High - rank Bitumin. | 1.3 | 33.3 | 66.7 | — | — | 84.1 | 5.3 | +60.5 |

TABLE I.—Continued.
Properties of Hand Separated Virrains.—Continued.

| Spec. No. | Locality. | Geological Age. | Rank. | Per- centage Ash. | Ash-free, Dry Basis. | | | | | | Percentage Volume Change on Car- bonising. |
|--------------|------------------------------|--------------------|----------------------------|-------------------------|--------------------------|-------------------------|--------------------------|-------------------------|----------------------------|-------------------------|--|
| | | | | | At 925° C. | | At 600° C. | | Per- centage Carbon. | Percentage Hydrogen. | |
| | | | | | Per- centage Vols. | Per- centage F.C. | Per- centage Vols. | Per- centage F.C. | | | |
| 458 | Redhead, N.S.W. | Perm. | Med. - rank Bitumin. | 2.6 | 36.9 | 63.1 | — | — | 83.7 | 5.7 | +81.0 |
| 459 | Belmont, N.S.W. . . | Perm. | Med. - rank Bitumin. | 1.8 | 37.6 | 62.4 | — | — | 83.4 | 5.4 | +21.0 |
| 288 | Wonthaggi, Victoria | Jur. | Med. - rank Bitumin. | 1.2 | 34.4 | 65.6 | 24.9 | 75.1 | 82.0 | 5.2 | 0.0 |
| 124 | Mt. Nicholas, Tasmania . . | Trias. | Med. - rank Bitumin. | 0.4 | 34.6 | 65.4 | 18.1 | 81.9 | 81.9 | 5.1 | —4.0 |
| 169 | Wallsend, N.S.W. | Perm. | Med. - rank Bitumin. | 2.1 | 34.4 | 65.6 | 26.4 | 73.6 | 81.3 | 5.0 | +2.0 |
| 174 | Liddell, N.S.W. . . | Perm. | Med. - rank Bitumin. | 3.0 | 40.9 | 59.1 | 31.5 | 68.5 | 81.0 | 6.8 | +58.8 |
| 172 | Rix Creek, N.S.W. | Perm. | Med. - rank Bitumin. | 0.4 | 38.9 | 61.1 | 25.9 | 74.1 | 80.9 | 5.1 | +49.0 |
| 181 | Kandos, N.S.W. | Perm. | Med. - rank Bitumin. | 0.6 | 36.3 | 63.7 | 27.6 | 72.4 | 80.8 | 5.1 | +46.0 |
| 212 | Mt. Mulligan, Queensland | Perm. | Med. - rank Bitumin. | 1.6 | 29.7 | 70.3 | 19.9 | 80.1 | 80.7 | 4.8 | —11.9 |
| 138 | Wonthaggi, Victoria | Jur. | Med. - rank Bitumin. | 1.0 | 38.2 | 61.8 | 27.8 | 72.2 | 80.3 | 4.9 | +2.1 |
| 186 | Seymour, Tasmania | Trias. | Low - rank Bitumin. | 2.7 | 36.5 | 63.5 | 27.0 | 73.0 | 80.0 | 5.0 | —12.8 |
| 461 | Swansea, N.S.W. | Perm. | Low - rank Bitumin. | 6.5 | 36.3 | 63.7 | — | — | 79.8 | 5.2 | +7.6 |
| 143 | Ipswich, Queensland. | Trias. | Low - rank Bitumin. | 5.0 | 35.5 | 64.5 | 26.1 | 73.9 | 79.1 | 5.2 | +2.8 |
| 209 | Callide, Queensland | Jur. | Sub-Bitumin. | 1.8 | 36.8 | 63.2 | 26.6 | 73.4 | 77.9 | 4.8 | —24.7 |
| 317 | Collie, Western Australia | Perm. | Sub-Bitumin. | 2.4 | 32.9 | 67.1 | — | — | 76.6 | 5.9 | — |
| 120 | Collie, Western Australia | Perm. | Sub-Bitumin. | 1.9 | 34.7 | 65.3 | 29.7 | 70.3 | 74.8 | 4.9 | —24.5 |
| 304 | Leigh Creek, South Australia | Trias. | High - rank Brown Coal. | 3.8 | 36.2 | 63.8 | 30.6 | 69.4 | 74.5 | 4.5 | —22.4 |

TABLE I.—Continued.
Properties of Hand Separated Vitreous.—Continued.

| Spec. No. | Locality. | Geological Age. | Rank. | Per-centage Ash. | Ash-free, Dry Basis. | | | | | | Percentage Volume Change on Carbonising. |
|-----------|----------------------------------|-----------------|------------------------------------|------------------|----------------------|------------------|-------------------|------------------|---------------------|----------------------|--|
| | | | | | At 925° C. | | At 600° C. | | Per-centage Carbon. | Percentage Hydrogen. | |
| | | | | | Per-centage Vols. | Per-centage F.C. | Per-centage Vols. | Per-centage F.C. | | | |
| 296 | Benwerrin, Victoria | Tert. | High - rank Brown Coal. | 2.5 | 36.5 | 63.5 | 30.3 | 69.7 | 72.9 | 4.4 | —25.0 |
| 290-291 | Leigh Creek, South Australia | Trias. | High - rank Brown Coal. | 6.5 | 41.9 | 58.1 | 34.5 | 65.5 | 71.9 | 4.5 | —23.2 |
| 456 | Moosonee, Canada | Cret. | Med. - rank Brown Coal. | 2.7 | 51.6 | 48.4 | — | — | 69.8 | 5.4 | —42.2 |
| 457 | Bovey Tracey, England | Tert. | Med - rank. Brown Coal. | 1.9 | 54.4 | 45.6 | — | — | 69.6 | 5.6 | —40.5 |
| 88 | Berridale, N.S.W. | Tert. | Med. - rank Brown Coal. | 3.2 | 53.8 | 46.2 | 38.4 | 61.6 | 68.9 | 5.5 | —28.5 |
| 299 | Yallourn, Victoria | Tert. | Med. - rank Brown Coal. | 1.1 | 52.4 | 47.6 | 43.0 | 57.0 | 68.4 | 5.4 | —23.7 |
| 454 | Liblar, Germany | Tert. | Med. - rank Brown Coal. | 1.4 | 54.7 | 45.3 | — | — | 68.3 | 5.5 | —51.6 |
| 286 | Bacchus Marsh, Victoria | Tert. | Med. - rank Brown Coal. | 4.5 | 50.3 | 49.7 | 42.7 | 57.3 | 68.0 | 5.1 | —25.9 |
| 136 | Yallourn, Victoria | Tert. | Med. - rank Brown Coal. | 1.8 | 60.1 | 39.9 | 41.8 | 58.2 | 67.4 | 4.3 | —24.5 |
| 142 | Kiandra, N.S.W. | Tert. | Brown Coal. Low - rank Brown Coal. | 0.6 | 62.0 | 38.0 | 51.7 | 48.3 | 66.3 | 6.1 | —28.7 |
| 298 | Kerguelen Island, Antarctica. | Tert. | Low - rank Brown Coal. | 7.1 | 52.5 | 47.5 | 44.2 | 55.8 | 63.8 | 5.1 | —23.0 |
| 283 | Kelso, Tasmania | Mioc. | Low - rank Brown Coal. | 0.5 | 55.3 | 44.7 | 45.3 | 54.7 | 63.4 | 5.1 | —33.7 |
| 455 | Cologne, Germany | Tert. | Low - rank Brown Coal. | 1.8 | 64.6 | 35.4 | — | — | 62.5 | 5.9 | —50.1 |
| 104 | Kiandra, N.S.W. | Tert. | Low - rank Brown Coal. | 0.4 | 76.4 | 23.6 | 62.8 | 37.2 | 59.2 | 6.1 | —21.6 |
| 453 | Haltern, Germany | Tert. | Peat. | 0.3 | 87.7 | 12.3 | — | — | 58.4 | 7.3 | —66.0 |
| 282 | <i>Euc. corymbosa</i> , Victoria | Contemp. | — | 0.1 | 82.1 | 17.9 | 72.6 | 27.4 | 52.1 | 5.6 | —38.8 |
| 75 | Potts Point, N.S.W. | Pleist. | Peat. | 5.1 | 75.0 | 25.0 | 69.7 | 30.3 | 51.3 | 5.7 | —31.6 |

series was carried out, and results (see Table 1) recorded as positive values where expansion took place, and negative values where contraction occurred.

Results with a high degree of reproducibility were obtained for the materials which underwent contraction, and also for most of those which showed expansion. However, some difficulty was experienced with vitrain of maximum swelling properties, as expansion was so great in some cases that the tube was of insufficient length to accommodate the coke. For these vitrains, which contained 85% to 88% carbon and gave expansions of more than 100%, a depth of 0.3 inch of the granular material was filled into the tube before carbonisation, enabling expansion results to be obtained. This introduced a variation in the conditions of carbonisation for a limited number of the strongly swelling vitrains, but their expansion was so great compared with all other members of the metamorphic series that discrepancies due to varied experimental conditions could not materially influence the general significance of results obtained.

After each test, the carbonised product was carefully removed from the tube and observations made as to its character. It was then crushed, where necessary, and sieved and graded as described earlier in the preparations of the vitrains. Some interesting features were noted in comparing the general nature of the granular samples of the vitrains with that of their carbonised products, and these observations are described later in this paper.

The residues from the carbonisation tests were saturated in preparation for determination of maximum inherent moisture, by boiling the granular material in water under reflux for one hour and then allowing it to stand in air-free water, in a tightly sealed test tube, for at least four days. Maximum inherent moisture was then determined in the same way as for the saturated vitrains. Behaviour of the carbonised products during removal of adherent moisture was exactly similar to that of the vitrains, except for cokes of strongly swelling vitrains which took a longer time to reach apparent dryness. Results for moisture determinations of the carbonised products (see Table 2) could be reproduced with the same degree of accuracy as those obtained for vitrains.

NOTES ON CHEMICAL PROPERTIES OF VITRAINS.

The selected materials range in carbon from 51.3% for a Pleistocene peat to 97.3% for the Rhode Island anthracite: the highest carbon determined for an Australian vitrain being 91.5%, which was obtained for a semi-anthracite from Mittagong, N.S.W. In this instance, anthracitisation is directly attributable to local igneous alteration by a sill. In general, there is a notable lack of true anthracite coals in Australian coalfields, due to the absence of widespread igneous alteration or folding of the Permian coal measures.

Hydrogen values obtained for the complete series vary between limits of 2.0% and 7.3%. Raistrick and Marshall found that a series of vitrains from American coals ranged from 5.1% to 6.0% hydrogen. Their materials, varying from 55% to 90% carbon, were all from American coalfields, whereas materials used in the present work came from widely scattered areas in different countries.

In a more detailed study of the constitution of vitrains from American coals, Marshall (1943) obtained results which present an interesting comparison with hydrogen values obtained for Australian vitrains. For the American series with a variation of 55.6% to 87.8% carbon it was found that hydrogen varied within limits of 4.6% and 6.0%. These figures were obtained from analyses of sixty-six samples of vitrain and it was noted that 95.5% of all members of the series had a hydrogen content between 5% and 6%. Hydrogen determined for Australian vitrains in the present investigation varies between limits of 4.4% and 6.8% for a similar carbon range (51.3% to 88.0%). This group contains thirty-four different samples but only 61.8% of these vitrains had a

hydrogen content between 5% and 6%; that is, a little more than half of the materials conformed to the variation determined by Marshall. Of the remainder, 29.4% had a hydrogen content of less than 5%, and the rest (8.8% of the series) had more than 6% hydrogen. Considering hydrogen content of Australian vitrains of all ranks, from 51.3% to 91.6% carbon, limits of hydrogen range from 3.3% to 6.8%, with only 58% of the vitrains analysed having a hydrogen content between 5% and 6%; from which it would appear that the proportion of hydrogen in Australian vitrains may vary over a considerably wider range of values than that determined for American vitrains. This contrast in proportions of hydrogen in vitrains from coals of the Northern and Southern Hemispheres may be the result of different environmental conditions of coalification or it may indicate fundamental differences in the nature of the original coal-forming constituents. It suggests that the plant material from which Australian coals were derived was of greater, or different, variety to that which gave rise to the American coals.

Standard proximate analyses at 925° C. (see Table 1) of all members of the vitrain series confirms the well-established continuous variation of volatile content with rank. Actual values range from a minimum of 3.8% for the Rhode Island material to a maximum of 87.7% for a German peat. Volatile yields calculated from low-temperature carbonisation of a selected number of the vitrains shows the same general increase in volatiles with increase in rank. However, actual values obtained for volatiles were much lower at the lower temperature. In plotting volatiles at 925° C. and at 600° C. against carbon, two distinct zones are obtained, the volatiles determined at the higher temperature falling in the upper zone. An examination of the differences in volatile contents obtained at the different temperatures shows that the increase in values at the higher temperature is not constant, and has no relationship to the rank of the vitrain from which it was obtained. Actual increases vary between limits of 3.9 and 18.3%.

Ash values for the vitrains are generally low, ranging from 0.1% to 6.0% with an overall average of 2.8% for the whole series; exceptions are the high ash values obtained for the Rhode Island anthracite and the Currabubula (N.S.W.) material, neither of which, however, was included in the preliminary acid washings. The anthracite, as already mentioned, cannot be regarded as a pure vitrain and the Currabubula material came from an area closely associated with igneous intrusion, producing an exceptionally high-ash coal.

NATURE OF THE CARBONISED PRODUCTS.

The carbonised residues of the granular vitrains fall into two distinct groups, which for the purpose of this paper will be referred to as *chars* and *cokes*. The chars are the non-coherent residues and the cokes are the coherent residues. Since all members of the metamorphic series are represented the nature of the carbonised residues varies considerably. Cokes are formed from vitrains of 79% to 89% carbon. Where carbon of the vitrain lies between 83% and 89%, a completely fused coke is formed in which no trace remains of the original individual grains. Two types of completely fused coke are recognisable and are described as *bubbly fused coke* and *dense fused coke*. The former is a coarsely porous or intumescenced coke and the latter is more finely porous and rather compact. Their formation does not seem to depend on the carbon content within this particular carbon range, nor does it seem to be related to the actual percentage of volatiles. However, the formation of bubbly fused coke is directly related to bulk-volume changes on carbonisation and is probably associated with the plastic properties of the vitrain during thermal decomposition.

Where the carbon of the vitrain ranges between 79% and 83%, the form of the carbonised residue varies greatly, this being in the nature of a transition

zone between the chars and the cokes, both of which are represented. Cokes of this group are typically partly fused or granular with the original grains distinguishable though they have become rounded or globular. Two types of granular cokes are distinguished and described as *strongly coherent granular coke* and *weakly coherent granular coke*, the distinction, as the terms suggest, being based on the degree of coherency of the individual grains.

Chars are formed from vitrains of both higher and lower rank than those which produce cokes. The chars formed from vitrains of sub-bituminous or lower rank (i.e. 79% carbon or less) will be referred to as *low-rank chars*, and those formed from vitrains on the high-rank, or anthracite, side of the coking vitrains (i.e. higher than 89.2% carbon) will be termed *high-rank chars*. Both low-rank and high-rank chars are completely non-coherent but it will be seen later that they are further distinguished by differences in their ultra-fine structure. It was noted that chars formed from vitrains which were originally bright have a brighter lustre than the vitrains from which they were formed. This was observed in chars from vitrains of both sub-bituminous and anthracite rank. However, vitrains from the brown coals and peats, which are dull in their original water-saturated condition and vary in colour from brown to black, form dull, black chars.

RELATION OF BULK-VOLUME CHANGES ON CARBONISATION TO RANK.

Results of bulk-volume changes on low-temperature carbonisations of granular vitrain, under free-swelling conditions as described earlier in this paper, are recorded in Table 1. Values obtained for percentage expansion or contraction were plotted against carbon as rank index, as illustrated in Figure 1. All points on the graph fall within a zone of fairly constant width, with a maximum in the region of the coking coals. The relationship so obtained illustrates variation in bulk-volume changes with rank. Where carbon of the vitrain is less than 79%, or exceeds 89%, contraction in bulk-volume takes place, with the formation of a char. Between 79% and 83% carbon, either contraction or expansion may take place, and where carbon lies between 83% and 89% expansion only is obtained.

On the low-rank side of the graph there is a suggestion of a zonal minimum in the region of 67% carbon. This corresponds very closely with the maximum in the moisture-rank relationship recorded by Dulhunty (1948) for the same vitrains, and it is suggested by that author that the maximum in moisture probably corresponds with the maximum degree of colloidal development attained during coalification. However, while the zonal maximum (Fig. 1) corresponds approximately with maximum colloidal development in the vitrain, the greatest contraction recorded (Vitrain No. 453) falls towards the low-rank side of the zonal minimum. This vitrain, having a contraction of 66%, is a peat wood from Haltern, Germany. It is perhaps significant that it undergoes least irreversible change on drying, and that maximum irreversible changes on drying are recorded (Dulhunty, 1948) for those materials falling in the region of the zonal minimum.

Vitrains of carbon content between 83% and 89% all show expansion on carbonisation, and the peak of this section of the zone lies at approximately 86% carbon. Expansion for these materials ranges from 21% to 598%, and the carbonised residues are all completely fused. There would seem to be some relationship between degree of expansion and maximum inherent moisture of the original vitrain. That the coking coals corresponded with the minimum in the moisture-carbon curve has long been recognised and more recently illustrated by Dulhunty (1948). From the results recorded in this paper (Fig. 1), it may be noted that for points lying towards the maximum of the expansion-carbon zone, where expansion values exceed 300%, moisture of the vitrains is

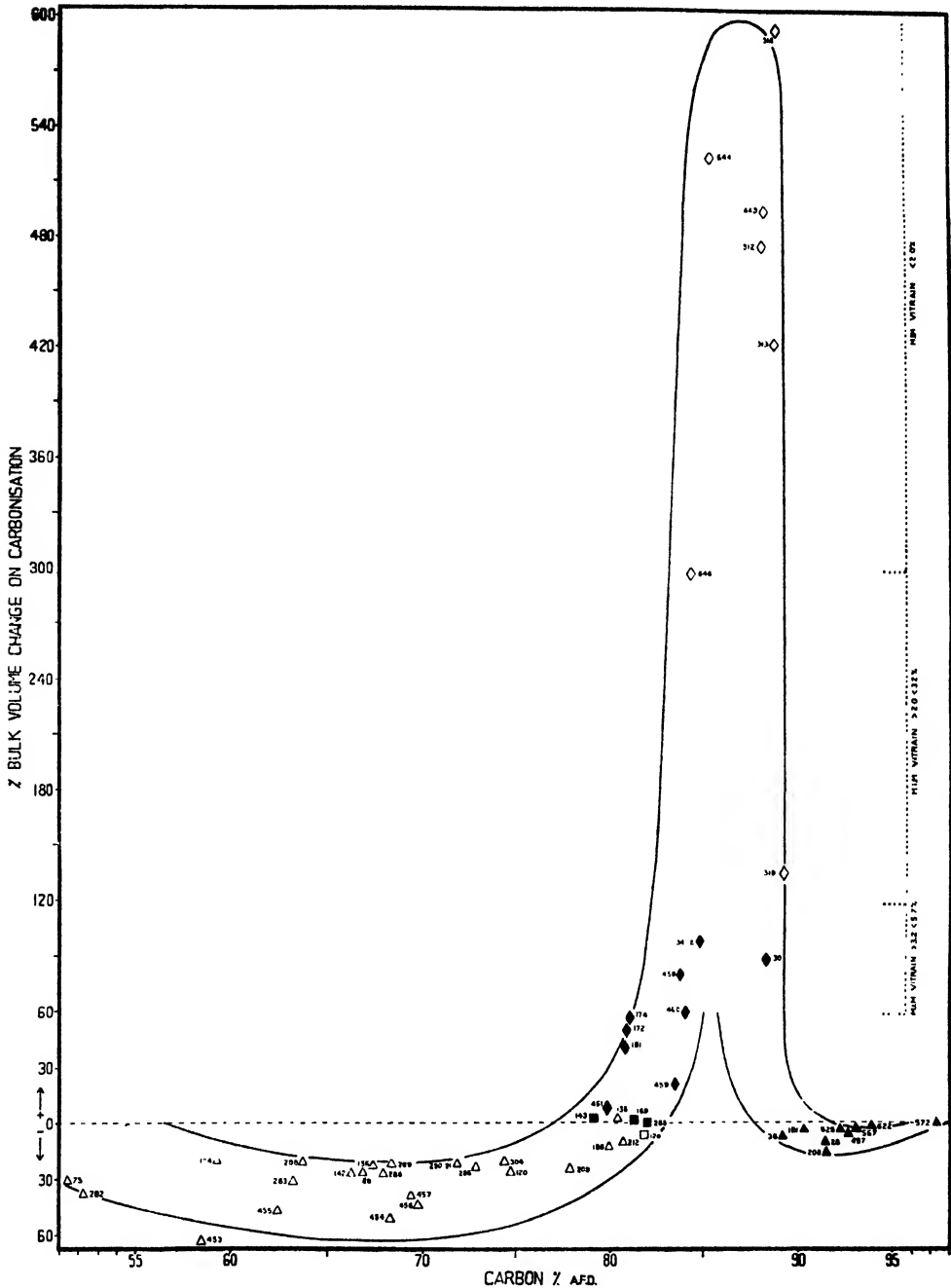


Fig. 1.—Relation of Rank to Bulk-Volume Changes on Carbonisation.
(For key to symbols see Fig. 2.)

2% or less. Where expansion exceeds 120% but not 300%, moisture values lie between 2% and 3.2%, and where expansion is greater than 60% but does not exceed 120%, moisture ranges between 3.2% and 5.7%. At the same

time, vitrains for which expansion values exceed 120% form bubbly fused cokes, and where expansion lies between 60% and 120%, dense fused cokes are formed.

In the 79% to 83% carbon group, where both expansion and contraction values are recorded, the carbonised residues are of various types. One vitrain (No. 288) of this group exhibits no change in bulk-volume on carbonisation. In this particular instance, tendencies to contract or expand are apparently compensating, although considerable changes occur in the ultra-fine structure of the material as will be illustrated later in this paper. Similar properties on carbonisation are also exhibited by the graphitic material, No. 572.

Considering again the chars formed from vitrains on both the high-rank and low-rank sides of the coking vitrains it was noted that in the case of the low-rank chars contraction in every instance exceeded 15%, while for the high-rank chars contraction did not exceed 15%.

In experiments designed to test the relation of free-swelling index to expansion of coal in experimental coke ovens for a series of coals ranging from low-volatile to high-volatile bituminous in rank, Selvig and Ode (1946) recorded measurements of percentage contraction and expansion on carbonisation. However, it was not possible to correlate their work with results obtained from vitrains of this series of similar rank, as materials used were pulverised rather than granular, and temperature ranges were not recorded for the experiments.

Cannon, Griffith and Hirst (1943) in their work on carbonisation of coals, also recorded measurements of contraction and expansion obtained on carbonising powdered coal which they related to heat of wetting phenomena. However, conditions of carbonisation were not comparable with those used in this work: time-temperature conditions were similar, but pulverised coal was used rather than granular vitrain and expansion and contraction measurements were not obtained under free-swelling conditions.

CHANGES IN PORE STRUCTURE IN VITRAIN ON CARBONISATION AND RELATION TO RANK.

As described earlier in this paper, maximum inherent moisture determinations were carried out on the carbonised residues of all vitrains in the series (see Table 2). In the case of vitrain, maximum inherent moisture depends on the natural condition of the micelle structure determined by metamorphic evolution in the earth's crust. Maximum inherent moisture of the carbonised product depends on the effects of carbonisation, but in each case it is presumably a measure of something closely related to the total volume of openings forming part of the ultra-fine structure, and small enough to lower the vapour pressure of water.

No definite relationship was established between maximum inherent moisture of the carbonised product and carbon of the vitrain from which it was formed. In many instances the moisture in the carbonised residue exceeded that of the corresponding vitrain, and in other instances was lower. It was found, however, that the difference between the moisture of vitrain and its carbonisation products is closely related to carbon content, or rank, of the vitrain. To illustrate this, the numerical difference between the moisture values for the vitrain and its carbonised product was expressed as a percentage of the moisture of the vitrain. Where moisture of the carbonised residue exceeded that of the vitrain, the increase was expressed as a positive value, and conversely, a decrease was expressed as a negative value (see Table 2). This percentage increase or decrease in moisture was then plotted against carbon determined for the original vitrain. A well-defined zonal relationship was established (see Fig. 2), the form of the zone being illustrated by lines

TABLE 2.
Maximum Inherent Moisture of Vitrains and Their Carbonisation Products.

| Spec. No. | Percentage Carbon A.F.D. Basis. | Percentage Maximum Inherent Moisture. Dry Basis. | | Actual Actual Difference. | Percentage Increase or Decrease. |
|--------------|--|--|------------------------|---------------------------------|---|
| | | Vitrain. | Carbonised Product. | | |
| 572 | 97.3 | 3.5 | 4.0 | +0.5 | +14.3 |
| 622 | 93.9 | 5.1 | 4.6 | -0.5 | -9.8 |
| 567 | 93.0 | 4.1 | 4.8 | +0.7 | +17.1 |
| 497 | 92.7 | 2.3 | 4.6 | +2.3 | +100.0 |
| 525 | 92.3 | 4.7 | 6.1 | +1.4 | +29.8 |
| 208 | 91.6 | 3.2 | 6.8 | +3.6 | +112.5 |
| 28 | 91.5 | 3.7 | 4.7 | +1.0 | +27.0 |
| 161 | 90.3 | 3.9 | 6.2 | +2.3 | +59.0 |
| 36 | 89.2 | 5.9 | 6.9 | +1.0 | +17.0 |
| 310 | 89.2 | 3.9 | 13.1 | +9.2 | +235.9 |
| 314 | 88.9 | 2.0 | 4.7 | +2.7 | +135.0 |
| 313 | 88.8 | 1.8 | 4.7 | +2.9 | +161.0 |
| 30 | 88.3 | 3.2 | 29.8 | +26.6 | +831.3 |
| 443 | 88.1 | 1.9 | 5.7 | +3.8 | +200.0 |
| 312 | 88.0 | 1.8 | 6.8 | +5.0 | +277.7 |
| 644 | 85.3 | 2.0 | 5.5 | +3.5 | +175.0 |
| 347-348 | 84.8 | 3.9 | 4.2 | +0.3 | +7.7 |
| 646 | 84.2 | 2.6 | 5.7 | +3.1 | +119.2 |
| 460 | 84.1 | 5.7 | 10.4 | +4.7 | +82.5 |
| 458 | 83.7 | 3.9 | 6.0 | +2.1 | +53.8 |
| 459 | 83.4 | 4.7 | 12.8 | +8.1 | +172.3 |
| 288 | 82.0 | 12.8 | 35.9 | +23.1 | +180.5 |
| 124 | 81.9 | 18.2 | 16.2 | -2.0 | -11.0 |
| 169 | 81.3 | 5.4 | 17.5 | +12.1 | +224.1 |
| 174 | 81.0 | 3.9 | 14.5 | +10.6 | +271.8 |
| 172 | 80.9 | 6.0 | 35.3 | +29.3 | +488.3 |
| 181 | 80.8 | 6.4 | 36.6 | +30.2 | +471.9 |
| 212 | 80.7 | 6.8 | 7.3 | +0.5 | +7.4 |
| 138 | 80.3 | 15.3 | 25.8 | +10.5 | +68.6 |
| 186 | 80.0 | 9.9 | 19.1 | +9.2 | +93.0 |
| 461 | 79.8 | 5.7 | 6.7 | +1.0 | +17.5 |
| 143 | 79.1 | 4.3 | 33.5 | +29.2 | +680.0 |
| 209 | 77.9 | 21.1 | 8.6 | -12.5 | -59.2 |
| 317 | 76.6 | 25.4 | 9.7 | -15.7 | -61.8 |
| 120 | 74.8 | 25.5 | 9.5 | -16.0 | -62.8 |
| 304 | 74.5 | 64.9 | 12.7 | -52.2 | -80.4 |
| 456 | 69.8 | 82.8 | 11.7 | -71.1 | -85.9 |
| 457 | 70.5 | 60.3 | 14.0 | -46.3 | -76.8 |
| 88 | 68.9 | 76.3 | 16.6 | -59.7 | -78.4 |
| 454 | 68.3 | 93.3 | 10.5 | -82.8 | -88.7 |
| 136 | 67.4 | 116.0 | 15.3 | -100.7 | -86.8 |
| 455 | 62.5 | 68.0 | 10.1 | -57.9 | -85.2 |
| 104 | 59.2 | 61.0 | 21.6 | -39.4 | -64.6 |
| 453 | 58.4 | 38.6 | 24.2 | -14.4 | -37.3 |

drawn at the approximate margins of the areas occupied by the points on the graph. This zone represents relationship of rank to moisture change on carbonisation.

All low-rank materials, that is vitrain of 79% carbon or less, show a decrease in moisture on carbonisation. At the low-rank extreme, a decrease in moisture of 37.3% is recorded for a peat wood of 58.4% carbon. As rank increases, the percentage decrease in moisture becomes greater till a zonal minimum is reached

at approximately 68% carbon. With further increase in rank the zone gradually rises, and at 79% carbon it becomes almost vertical, and all vitrains at this rank or higher show, with two minor exceptions, an increase in moisture on carbonisation. Between approximately 79% and 90% carbon there is a well-defined maximum, the peak of which is probably situated at about 86% carbon. Where carbon lies between 79% and 82%, that is, for vitrains of bituminous rank, the increase in moisture may be as much as 832%, or as little as 7.4%. A sharp reduction in moisture increase occurs at 90% carbon, and towards the anthracite end of the zone, increase in moisture does not exceed 115% and gradually lessens as carbon approaches 100%.

An interesting comparison may be made in the form of this zone and that obtained by Dulhunty (1948) for the maximum inherent moisture-carbon relationship of the same vitrains. The maximum in the moisture-carbon curve at 68% carbon, corresponds exactly with the zonal minimum in the relationship of rank to moisture change on carbonisation. However, the apparent peak, at 86% carbon, of the zonal maximum in this relationship (Fig. 2) is a little to the low-rank side of the minimum in the moisture-carbon curve which falls at about 88% carbon.

The zonal relationship of rank to moisture change on carbonisation is closely allied in form to that established for the relationship of bulk-volume change on carbonisation to rank (Fig. 1). In both instances zonal minima are established at 68% carbon and the peaks of the maxima are developed at 86% carbon approximately. Vitrains of 79% carbon and less show a decrease in moisture on carbonisation and a contraction in bulk-volume. Between 79% and 83% carbon, with one exception, all materials show an increase in moisture, but changes in bulk-volume may be either contraction or expansion. Where vitrains are of coking bituminous rank, that is, between 83% and 89% carbon, maximum expansion is recorded and all vitrains of this group show an increase in moisture on carbonisation. An interesting feature in the comparison of these relationships is the increase in moisture in vitrains of 89% carbon or more all of which suffer contraction in bulk-volume on carbonisation.

Earlier in this paper a distinction is drawn between low-rank and high-rank chars. The relationship of moisture change on carbonisation to rank shows that a further distinction may be drawn on the basis of properties related to the ultra-fine structure of the chars. The carbonised residues of low-rank vitrains all show a decrease in moisture exceeding 37%, while the high-rank chars, with one exception, show an increase in moisture. An increase in moisture on carbonisation is also shown by any vitrain which produces a completely fused coke. From the illustration in Fig. 2 it will be seen that the greatest increase in moisture is obtained for dense fused cokes, and not for bubbly fused cokes which emphasizes that the bubbly structure is a macroscopic feature.

It is interesting and perhaps significant to note that the formation of low-rank chars is accompanied by a decrease in maximum inherent moisture whilst the formation of high-rank chars involves an increase. The plastic properties of coking coals during carbonisation have long been recognised and in vitrain undergoing plastic deformation it is not difficult to visualise the necessary rearrangement of the ultra-fine structure required to give an increase in moisture on carbonisation. Yet moisture increases are obtained in the case of the high-rank vitrains which do not undergo plastic deformation in the same way, but produce a char in which the identity of the original individual particles is retained.

From the study of heat of wetting and carbonisation, carried out by the British Coal Utilisation Research Association (Cannon, Griffith and Hirst, 1943) on coals varying in rank from high volatile bituminous through to medium volatile anthracites, it was concluded that the micelle structure, or something related to it, persists throughout carbonisation. It was also concluded that

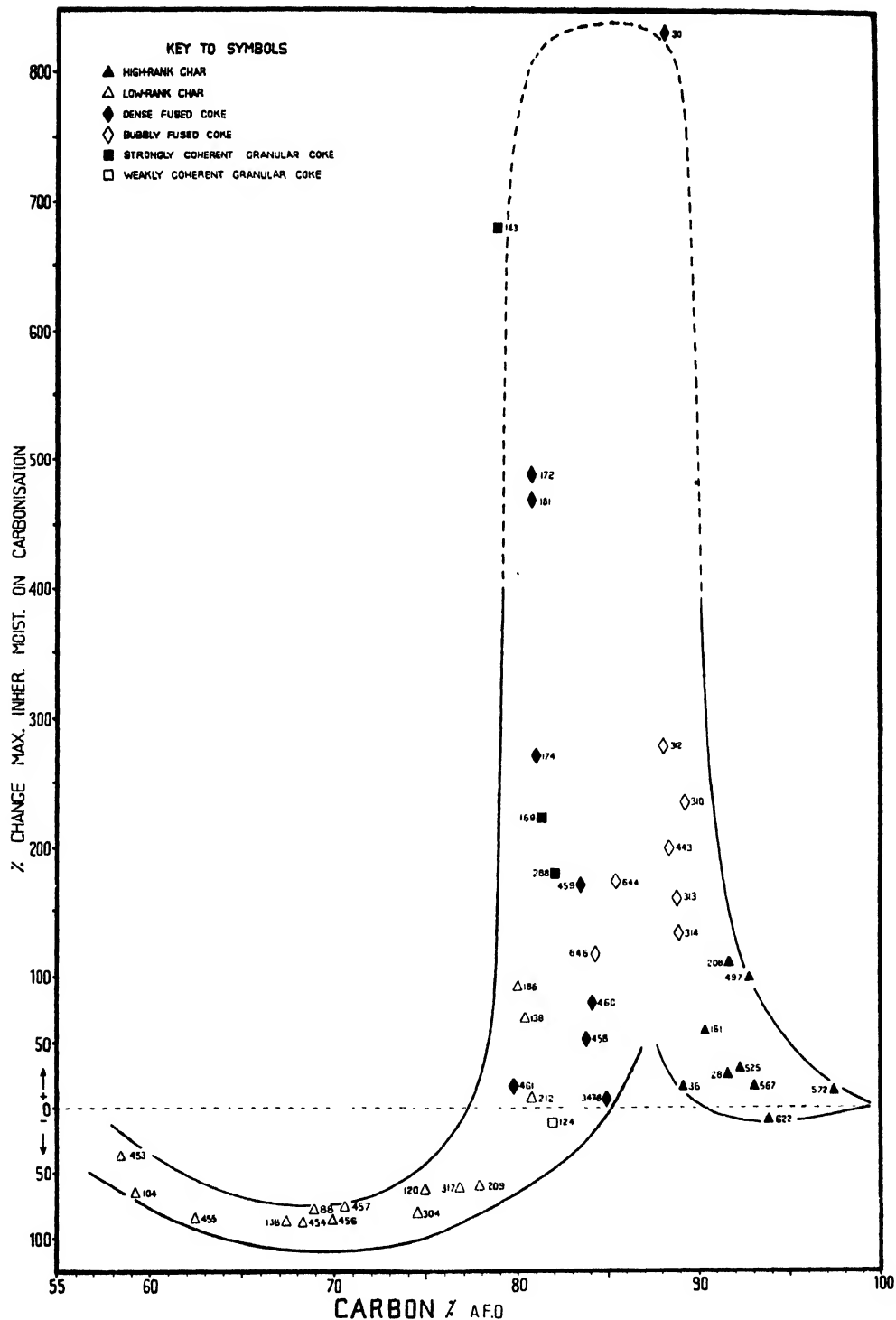


Fig. 2.—Relation of Rank to Per Cent. Change in Maximum Inherent Moisture on Carbonisation.

there is no great change in the internal surface area in so much that coals of small surface give carbonised products of small surface, and those with large surface give carbonisation products with large internal surface.

In so far as maximum inherent moisture determinations may be considered a measure of total internal volume of the coal substance (King and Wilkins 1943), then broadly the effects of carbonisation on the internal volume of the vitrains are as follows :

- (1) Volume decreases if the vitrain contains less than 79% carbon, or more significantly perhaps, if the material has not attained that critical stage in the process of coalification (Dulhunty, 1948) beyond which irreversible changes on drying do not take place.
- (2) Volume increases where carbon of the vitrain exceeds 79%, i.e. vitrain coalified beyond the stage at which irreversible changes take place on drying.

In the first case, carbonisation of the low-rank coals is accompanied by considerable loss of substance due to devolatilisation, and materials of this rank do not undergo plastic deformation during the process of carbonisation which produces a char. Reduction in internal volume then may be satisfactorily accounted for by the increased areas of contact between the micelle (with corresponding decrease in inter-micelle spaces) as suggested by Bangham (1943) and Bangham and Maggs (1943) to be the result of carbonisation. At the same time, these vitrains suffer a decrease in bulk-volume under free-swelling conditions of carbonisation.

The second group includes both the coking vitrains and those which give high-rank chars. The former give very great increases in internal volume, particularly vitrains from which dense fused cokes are formed. If, as heat of wetting determinations, carried out at various stages during the carbonisation of bituminous and anthracitic coals, and electrical conductivity measurements, would seem to so clearly indicate, the micelle structure or something related to it persists throughout carbonisation, it is difficult to account for the very large increases in internal volume recorded here for vitrains of similar rank and carbonised under similar conditions. The suggestion is offered that a new or supplementary pore structure is developed, dependent on the nature and rate of evolution of the volatiles and the degree of plasticity during carbonisation. In this structure the pores may be of such dimensions as to be inaccessible to the methanol molecule used in heat of wetting-surface area determinations, but accessible to the smaller water molecule used to measure internal volume. Alternatively, it is suggested that the original pore structure almost entirely disappears, being replaced by pores of greater radii which would increase internal volume but not internal area. That such a structure could result from gaseous emanations through a plastic medium during carbonisation is a possibility for consideration in the case of the coking vitrains, or those exhibiting intumescence, but it does not satisfactorily account for increases in internal volume obtained for vitrains producing high-rank chars. The latter do not undergo plastic deformation during carbonisation and volatile evolution is relatively insignificant; moreover, a decrease in *bulk-volume* accompanies an increase in *internal volume* for the high-rank chars. The elucidation of these apparent anomalies offers an interesting problem for further research.

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SUMMARY.

Vitrains of all ranks from the Southern Hemisphere show greater variation in hydrogen content than those from the Northern Hemisphere, suggesting differences in original plant materials. Volatile yields at 920° C. exceed those at 600° C. by a variable amount which cannot be related to rank. A zonal relationship exists between rank and bulk-volume changes on carbonisation with a minimum at 67% carbon and a maximum at 86% carbon. A similar relationship was established between rank and differences in capillary-held moisture of vitrain and its carbonisation products. These relationships indicate that vitrains of 79% carbon or less produce chars, or non-coherent residues, showing an overall contraction in bulk-volume exceeding 15% and holding less capillary-condensed moisture than the original vitrain. Where carbon of the vitrain is 79% and does not exceed 89.2%, a coke is formed which may show either contraction or expansion in bulk-volume but in which capillary-condensed moisture exceeds that of the original vitrain. A char is also formed from vitrains of 89.2% carbon or more, in which overall contraction in bulk-volume does not exceed 15% and in which the amount of capillary-condensed moisture exceeds that of the original vitrain.

THE AUSTRALIAN SOCIAL SERVICES CONTRIBUTION AND INCOME TAX ACTS, 1949.

By H. MULHALL.

Manuscript received, September 15, 1949. Read, October 5, 1949.

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I.

Professor H. S. Carslaw has examined in a series of papers the graduation of Australian taxation on individual incomes from the introduction of uniform taxation in 1942 to the Social Services Contribution and Income Tax Acts of 1947 which were relevant to the year ending June 30th, 1948. Since the appearance of his last paper (Carslaw, 1948) there have been two further reductions in taxation. It is now proposed to set out for the most recent Act the analysis given by Professor Carslaw for the Act of 1947. His notation is retained; the amount of tax and/or contribution on an income of £x is denoted by T pence.

The rate of tax on this income is denoted by $R\left(=\frac{T}{x}\right)$ with, if required, a suffix,

say R_1 or R_2 . The rebatable amount on the income is denoted by £A.

II.

The basic rate of contribution applying to a taxpayer entitled to no rebates is given by the formula

$$R_1 = 3 + \frac{3}{80}(x - 100), \text{ when } x \leq 500.$$

The maximum rate of 18 pence is reached at $x = 500$.

The amount of contribution payable is thus

$$T = x \left[3 + \frac{3}{80}(x - 100) \right].$$

The contribution commences at $x = 105$, but there is a proviso that no person shall pay a contribution greater than half the excess of his income over £104.

For taxpayers entitled to rebates on account of dependents, medical expenses, etc., the concessional rate is given by the formulæ

$$R_2 = \frac{3x-A}{100} \text{ when } x-A < 100$$

$$= 3 + \frac{3}{80}(x-A-100) \text{ when } 100 < x-A < 500.$$

$$= 18 \text{ when } x-A > 500.$$

When using these formulæ it should be noted that there is a special rebate for a taxpayer whose income does not exceed £350 and who has any dependents. This rebate is £50 when the income does not exceed £250, diminishing by £1 for every £2 by which the income exceeds £250, so that it vanishes at £350.

The following list shows the incomes at which liability to Social Services Contribution begins and those at which the maximum rate of 18 pence in the £ is reached.

| | £ |
|---|---------|
| Single person | 105-500 |
| Person with dependent wife | 201-650 |
| Person with dependent wife and one child | 284-750 |
| Person with dependent wife and two children | 318-800 |
| Person with dependent wife and three children | 351-850 |
| Person with dependent wife and four children | 401-900 |
| Person with dependent wife and five children | 451-950 |

III.

This section deals with Income Tax as distinct from Social Services Contribution, which must, of course, be added to the amounts calculated from the formulæ which follow to give the total amount payable. The formulæ refer to taxpayers entitled to no rebates.

Earned Income.

- (a) When $x \leq 500$,
 $T = 0.$

- (b) When $500 < x \leq 1000$,

$$T = (x - 500) \left[18 + \frac{24}{1000}(x - 500) \right]$$

$$= \frac{24}{1000}x^2 - 6x - 3000.$$

- (c) When $1000 < x \leq 2000$,

$$T = 15 \times 1000 + (x - 1000) \left[42 + \frac{2}{100}(x - 1000) \right]$$

$$= \frac{2}{100}x^2 + 2x - 7000.$$

- (d) When $2000 < x \leq 5000$,

$$T = 38 \cdot 5 \times 2000 + (x - 2000) \left[82 + \frac{1}{100}(x - 2000) \right]$$

$$= \frac{1}{100}x^2 + 42x - 47000.$$

(e) When $5000 < x \leq 10,000$,

$$\begin{aligned} T &= 82.6 \times 5000 + (x - 5000) \left[142 + \frac{2}{1000}(x - 5000) \right] \\ &= \frac{2}{1000}x^2 + 122x - 247,000. \end{aligned}$$

(f) When $x > 10,000$,

$$T = 117.3 \times 10,000 + 162(x - 10,000).$$

Income from Property.

(a) When $x \leq 350$,

$$T = 0.$$

(b) When $350 < x \leq 500$,

$$\begin{aligned} T &= (x - 350) \left[7.75 + (x - 350) \frac{5}{1000} \right] \\ &= \frac{5}{1000}x^2 + 4.25x - 2100. \end{aligned}$$

(c) When $500 < x \leq 1000$,

$$\begin{aligned} T &= 2.55 \times 500 + (x - 500) \left[28 + \frac{3}{100}(x - 500) \right] \\ &= \frac{3}{100}x^2 - 2x - 5225. \end{aligned}$$

(d) When $1000 < x \leq 2000$,

$$\begin{aligned} T &= 22.775 \times 1000 + (x - 1000) \left[58 + \frac{22}{1000}(x - 1000) \right] \\ &= \frac{22}{1000}x^2 + 14x - 13,225. \end{aligned}$$

(e) When $2000 < x \leq 5000$,

$$\begin{aligned} T &= 51.3875 \times 2000 + (x - 2000) \left[102 + \frac{8}{1000}(x - 2000) \right] \\ &= \frac{8}{1000}x^2 + 70x - 69,225. \end{aligned}$$

(f) When $5000 < x \leq 10,000$,

$$\begin{aligned} T &= 96.155 \times 5000 + (x - 5000) \left[150 + \frac{12}{10000}(x - 5000) \right] \\ &= \frac{12}{10000}x^2 + 138x - 239,225. \end{aligned}$$

(g) When $x > 10,000$,

$$T = 126.0775 \times 10,000 + 162(x - 10,000).$$

IV.

It will be noticed that all the amounts in Section III (except for $x > 10,000$) are expressed in the form $ax^2 + bx + c$. The total amount payable (Income Tax plus Social Services Contribution) is also expressible in this form. Following

Carslaw's notation, if $T(x)$ denote the amount payable on an income of $\pounds x$, the x th \pounds pays an amount $T(x) - T(x-1)$, an expression of the form $a(2x-1) + b$. It is this increment which interests the taxpayer concerned about the amount of tax payable on additional income.

Earned Income.

There is no income tax on incomes not exceeding $\pounds 500$; the amount of contribution payable is

$$\begin{aligned} & x \left[3 + \frac{3}{80}(x-100) \right] \\ &= \frac{3}{80}x^2 - \frac{3}{4}x. \end{aligned}$$

The x th \pounds therefore pays $\frac{3}{80}(2x-1) - \frac{3}{4}$ pence. For example, at $x=400$ the amount of contribution is 5700 pence; the rate $\left(\frac{T}{x}\right)$ is 14.25 pence per \pounds . The 401st \pounds pays 29.2875 pence.

When x exceeds 500, the Social Services Contribution remains 18 pence per \pounds . The total amount payable on an income of $\pounds x$ is thus

$$ax^2 + bx + c + 18x$$

the values of a, b, c being those given in Section II for the various income ranges. The amount payable on the x th \pounds is $[a(2x-1) + b + 18]$ pence. For any given range, these increments form an arithmetic progression with common difference $2a$.

Thus, the 501st \pounds pays 36.024 pence; the common difference for the range is 0.048 and the 1000th \pounds pays 59.976 pence.

The 1001st \pounds pays 60.02 pence; the common difference is 0.040 and the 2000th \pounds pays 99.98 pence.

The 2001st \pounds pays 100.01 pence; the common difference is 0.020 and the 5000th \pounds pays 159.99 pence.

The 5001st \pounds pays 160.002 pence; the common difference is 0.004 and the 10,000th \pounds pays 179.999 pence.

The 10,001st \pounds pays 180 pence. This is the maximum rate.

It is interesting to note that the 3001st \pounds pays 120.02 pence. For a taxpayer without dependents it is only on income in excess of $\pounds 3000$ that more than half of every additional pound is paid out in tax.

Income from Property.

For property incomes, tax begins at $\pounds 350$, before the Social Services Contribution has reached the maximum rate. From the expressions for Tax and Contribution, the following formula for the total amount payable is obtained

$$\frac{42.5}{1000}x^2 + 3.5x - 21,000 \quad 350 < x \leq 500.$$

The 351st \pounds pays 33.2925 pence; the common difference is 0.085 and the 500th \pounds pays 45.9575 pence.

For incomes in excess of $\pounds 500$ the calculation of the increment is carried out in the same way as for earned income, the values of a and b corresponding

to a given value of x being ascertained from the formulæ of Section III. For example, if $1000 < x < 2000$, $a=0.022$, $b=14$. The 1001st £ pays a total of $58.022+18=76.022$ pence; this increment increases by 0.044 pence per £ and the 2000th £ pays 119.978 pence. For property incomes the increment exceeds 10/- in the £ when x exceeds 2000. The maximum rate of 180 pence is again reached at incomes of £10,000, but the approach to this rate is more rapid than for earned income.

V.

Figure 1 shows the total amount (Tax and Contribution) by each £ of income received in the year ending June 30th, 1950, for a taxpayer entitled to no rebates. The procedure followed is that given by Carslaw.

If the total amount payable has the form ax^2+bx+c , the amount paid by the x th £ has been shown to be $[a(2x-1)+b]$ pence. Thus the line $y=2ax+b$ has for the ordinate at $x-\frac{1}{2}$ the amount of tax on the x th £. For earned income

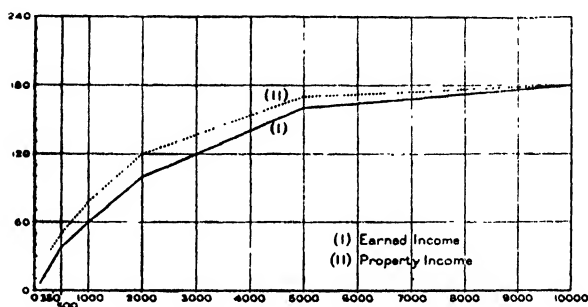


Fig. 1.

the graph will be made up of line segments corresponding to the ranges (a) to (f) of Section III. We shall assume $x > 105$. The equations of the lines are given below.

$$(a) \quad x \leq 500$$

$$y = \frac{3}{40}x - \frac{3}{4}$$

$$(b) \quad 500 < x \leq 1000$$

$$y = \frac{48}{1000}x + 12$$

$$(c) \quad 1000 < x \leq 2000$$

$$y = \frac{40}{1000}x + 20$$

$$(d) \quad 2000 < x \leq 5000$$

$$y = \frac{20}{1000}x + 60$$

$$(e) \quad 5000 < x \leq 10,000$$

$$y = \frac{4}{1000}x + 140.$$

When $x > 10,000$ the constant maximum rate is given by $y=180$.

Similarly, the lines making up the graph relevant to Property Income are :

$$(a) \quad x \leq 350$$

$$y = \frac{75}{1000}x - \frac{3}{4}$$

$$(b) \quad 350 < x \leq 500$$

$$y = \frac{85}{1000}x + 3.5$$

$$(c) \quad 500 < x \leq 1000$$

$$y = \frac{60}{1000}x + 16$$

$$\begin{aligned}
 (d) \quad 1000 < x < 2000 & \quad y = \frac{44}{1000}x + 32 \\
 (e) \quad 2000 < x < 5000 & \quad y = \frac{16}{1000}x + 88 \\
 (f) \quad 5000 < x < 10,000 & \quad y = \frac{2 \cdot 4}{1000}x + 156 \\
 (g) \quad x > 10,000 & \quad y = 180.
 \end{aligned}$$

It will be observed that there is an irregularity in the graph describing the amount payable on property income. This results from the commencement of Income Tax at $x=350$, before the Contribution rate has reached its maximum value.

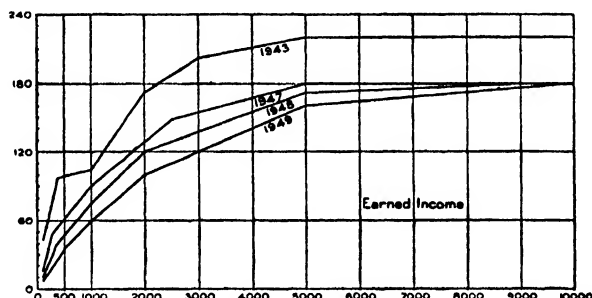


Fig. 2.

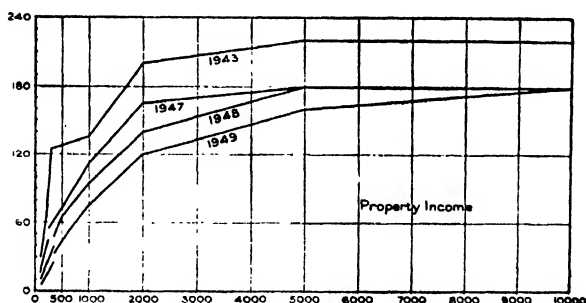


Fig. 3.

Figures 2 (Earned Income) and 3 (Property Income) compare the rates prevailing in 1943 (the year of maximum taxation), 1947, 1948 and 1949. Figure 2 shows that for incomes up to £1000 per annum it is no longer true that incentive to increase output is destroyed by the excessive taxation on additional earnings (overtime, etc.), the additional tax, even for a taxpayer without dependents, being always less than five shillings in the £.

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Carlsaw, H. S., 1947. The Australian Social Services Contribution and Income Tax Acts, 1947. *The Economic Record*, pp. 3-11. References to papers on the earlier Acts are given in this paper.

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STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART I. TETRAMMINE PLATINUM (II) FLUORIDES.

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Manuscript received, September 7, 1949. Read, October 5, 1949.

A survey of the literature on platinum and fluorine indicates very little is known on the chemistry of platinum fluorides. Platinum (II) and platinum (IV) fluorides have been reported (Mellor, 1937). Fluoroplatinates (IV) of sodium, potassium and ammonium have also been prepared (Mellor, 1937), K_2PtF_6 (Schlesinger and Tapley, 1924) being a pale yellow crystalline compound sparingly soluble in water, in which it is relatively stable. Among the platinum complexes, Hedin (1886) reported the possible existence of difluoro dipyridine platinum (II). $[\text{Pt}(\text{NH}_2\text{OH})_4](\text{HF}_2)_2 \cdot 2\text{H}_2\text{O}$ has also been prepared (Goremykin, 1944).

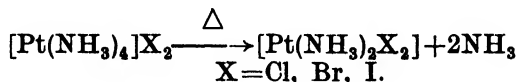
In this investigation the fluorides and hydrogen fluorides of the complex ion $[\text{PtA}_4]^{++}$ have been prepared ($\text{A}=\text{NH}_3$, $\text{C}_5\text{H}_5\text{N}$; $2\text{A}=\text{C}_2\text{H}_4(\text{NH}_2)_2$). These are all colourless substances, crystallising in well-formed crystals from water or aqueous acetone, often with water of crystallisation, part of which is lost on drying over P_2O_5 . They were all readily soluble in water, the solution of the hydrogen fluorides having a distinctly acid reaction and liberating CO_2 from carbonates. The ion $[\text{PtA}_4]^{++}$ was quite stable in the presence of excess hydrofluoric acid, and the salts could be evaporated with 46% acid at the boiling point without decomposition.

Hydrogen fluorides prepared by evaporation to dryness in this fashion yielded salts of the type $[\text{Pt}(\text{NH}_3)_4](\text{HF}_2)_2$. These salts were stable in a dry atmosphere but exposure to air resulted in the loss of HF, glass in the immediate vicinity being etched. The effect was greatest with the ethylenediamino and least with the pyridino compounds. Further, when $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2](\text{HF}_2)_2$ was dissolved in aqueous hydrofluoric acid solution and crystallised by the addition of acetone, the compound $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\text{HF}_2 \cdot \text{F} \cdot \text{H}_2\text{O}$ was obtained, in which one HF_2^- anion had been replaced by a $\text{F}^- \cdot \text{H}_2\text{O}$ group. The same tendency was probably operative in the case of the $[\text{Pt}(\text{NH}_3)_4](\text{HF}_2)_2$ salt. Whenever crystallised from aqueous acid solution by the addition of acetone, the compound contained less F than required by formula. It is possible that a continuous series of compounds, containing mixed anions, exist intermediate between $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2](\text{HF}_2)_2$ and $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\text{F} \cdot \text{H}_2\text{O}$, in which the H_2O is strongly held by the hydrogen bonds to the F^- anion, so that the HF_2^- can be replaced by $\text{F}^- \cdots \text{H}-\text{O}-\text{H}$ without alteration to the structure.

The stability of the complex ion towards hydrofluoric acid contrasts strongly with its behaviour towards other halogen acids. Thus it is well known that the addition of hydrochloric acid to $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ results in the formation of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. That this difference cannot be attributed wholly to the fact that hydrofluoric acid is a comparatively weak acid is supported by the fact that $[\text{Pt}(\text{NH}_3)_4]\text{I}_2$ passes readily to $[\text{Pt}(\text{NH}_3)_2\text{I}_2]$ on boiling the aqueous solution.

Thus it must be assumed that the lack of reaction between $[\text{Pt}(\text{NH}_3)_4]^{++}$ and HF is due in some measure to the reluctance of Pt and F to form a covalent bond.

The stability of these compounds to heat is in process of investigation in order to compare with the general reaction of the type



Preliminary experiments on the behaviour of the cis and trans diammine bases, $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]$ etc., with hydrofluoric acid have indicated anomalous results. The results of these experiments will be reported in later papers in this series.

EXPERIMENTAL.

(All operations involving fluorides were carried out in platinum or paraffin vessels. The hydrofluoric acid used was A.R. quality (General Chemical Co., U.S.A.) with analysis 0.15% H_2SiF_6 (max.).

Tetrammine Platinum (II) Hydrogen Fluoride.

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ was prepared ("Inorganic Syntheses", II, 250).

Found: Pt, 55.6%; Cl, 20.3%. Calculated: Pt, 55.4%; Cl, 20.1%.

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (0.5 g.) was converted to a solution of $[\text{Pt}(\text{NH}_3)_2](\text{OH})_2$ with Ag_2O . After separation of AgCl and excess Ag_2O , the solution was acidified with excess HF, evaporated to near dryness on the water bath and finally dried in an air oven at about 70° C. until excess HF expelled. The residue was further dried *in vacuo* over CaCl_2 for several days. Under microscope, the compound consisted of clear, colourless quadrilateral plates with angles $\neq 90^\circ$. The compound was readily soluble in water, the solution having a distinctly acid reaction. Yield, 0.4 g. On exposure to air the compound lost HF, glass in the vicinity being etched.

Found: Pt, 56.9%; F, 21.7%.

$[\text{Pt}(\text{NH}_3)_2](\text{HF})_2$ requires Pt, 57.2%; F, 22.3%.

The method was varied by crystallising the salt from aqueous hydrofluoric solution with acetone. The compound crystallised in long thin needles.

Found (dried over P_2O_5): Pt, 57.1%; F, 20.3%.

Recrystallised aqueous HF+acetone, Pt, 57.3%; F, 20.5%.

Tetrammine Platinum (II) Fluoride 1.5 Hydrate.

$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$, 5.0 g., was converted to a solution of the corresponding hydroxide as before and the solution divided into two equal portions. One portion was converted to the solid hydrogen fluoride and the second portion then added. After evaporation the compound was crystallised by the addition of acetone. Recrystallised from aqueous acetone. Yield, 4.1 g. $[\text{Pt}(\text{NH}_3)_4]\text{F}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ was readily soluble in water, the solution having an alkaline reaction (litmus). From aqueous acetone the compound was obtained in very fine white microcrystals. On heating at 100° C. only $1\text{H}_2\text{O}$ is lost, the remaining $\frac{1}{2}\text{H}_2\text{O}$ being held strongly in the compound, probably by hydrogen bonds to the fluoride ion.

Found (on air-dry material): Pt, 59.9%; F, 11.1%; H_2O , 5.8% (loss in one hour at 100° C.).

$\text{Pt}(\text{NH}_3)_4\text{F}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ requires Pt, 59.5%; F, 11.6%. Loss for $1\text{H}_2\text{O}$, 5.5%.

Tetrapyridine Platinum (II) Hydrogen Fluoride 6-Hydrate.

$[\text{Pt}(\text{C}_5\text{H}_4\text{N})_4]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (Drew, Pinkard, Wardlaw and Cox, 1932) was recrystallised from aqueous acetone.

Found: Pt, 30.7%; Cl, 11.1%. Calculated: Pt, 30.7%; Cl, 11.1%.

3.0 g. were treated in the same manner as described for the corresponding tetrammino compound. From aqueous HF solution $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4](\text{HF})_2 \cdot 6\text{H}_2\text{O}$ crystallised in white opaque rectangular plates on the addition of acetone; yield, 1.0 g. The compound was very soluble in water, the solution having a distinctly acid reaction. Over P_2O_5 , $5\frac{1}{2}\text{H}_2\text{O}$ are lost, the remaining $\frac{1}{2}\text{H}_2\text{O}$ being lost on heating to 100°C . The dehydrated salt very slowly absorbs H_2O from the air. On exposure to air the salt slowly loses HF, this effect being less than with the corresponding tetrammino salt.

Found (on air-dry material): Pt, 28.0%; F, 10.7%; H_2O , 14.1%, 14.2% (loss *in vacuo* over P_2O_5), 15.4% (loss in one hour at 100°).

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4](\text{HF})_2 \cdot 6\text{H}_2\text{O}$ requires Pt, 28.0%; F, 10.9%. Loss for $5\frac{1}{2}\text{H}_2\text{O}$, 14.2%; loss for $6\text{H}_2\text{O}$, 15.5%.

Tetrapyridine Platinum (II) Fluoride 9-Hydrate.

5.0 g. of the corresponding chloride were treated by the method employed for the corresponding tetrammino compound. From the aqueous solution $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2 \cdot 9\text{H}_2\text{O}$ crystallised in clear colourless cubes and octahedra on the addition of acetone. Recrystallised from aqueous acetone. Yield, 3.3 g. The compound was readily soluble in water, giving a distinctly alkaline reaction with litmus paper. The salt readily loses $6\text{H}_2\text{O}$ on drying over P_2O_5 . The trihydrate is stable to 100° , at which temperature decomposition is commencing, pyridine being lost and the residue turning yellow. The trihydrate rapidly takes up six moles of H_2O on exposure to air.

Found (air-dry material): Pt, 27.6%; F, 5.3%; H_2O , 15.1%, 15.7% (loss *in vacuo* over P_2O_5).

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2 \cdot 9\text{H}_2\text{O}$ requires Pt, 27.4%; F, 5.3%. Loss for $6\text{H}_2\text{O}$, 15.2%.

Bis(ethylenediamine) Platinum (II) Hydrogen Fluoride.

Bis(ethylenediamine) platinum (II) chloride was prepared by the action of aqueous ethylenediamine on K_2PtCl_4 , filtering the insoluble $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2\text{Cl}_2]$ and dissolving in aqueous ethylenediamine. $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]\text{Cl}_2$ crystallised on the addition of alcohol-acetone. Recrystallised from hot water.

Found: Pt, 50.5%; Cl, 18.3%. Calculated: Pt, 50.5%; Cl, 18.4%.

1.0 g. was converted at the corresponding hydroxide and the solution evaporated with excess HF in the same manner as described for the corresponding tetrammino compound. After evaporation on the water bath the residue was baked in an air oven at 110°C . Yield, 1.1 g. Examined under microscope, the material consisted of broken, jagged, colourless crystals. The compound was slightly deliquescent and readily soluble in water, the solution having a distinctly acid reaction. On exposure to air HF is readily lost, glass in the vicinity being badly etched.

Found (material dried over CaCl_2): Pt, 49.5%; F, 18.9%.

$[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2](\text{HF})_2$ requires Pt, 49.6%; F, 19.3%.

Bis(ethylenediamine) Platinum II Fluoride Hydrogen Fluoride 1-Hydrate.

A solution of the hydrogen fluoride, prepared as above, in aqueous hydrofluoric acid, was crystallised by the addition of acetone. The compound crystallised in clear colourless rectangular plates. The dry compound gave an acid reaction with moist litmus paper.

Found (material dried over P_2O_5): Pt, 49.8%; F, 13.8%.

$[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]_{\text{HF}_2}^{\text{F} \cdot \text{H}_2\text{O}}$ requires Pt, 49.9%; F, 14.5%.

Bis(ethylenediamine) Platinum (II) Fluoride 2-Hydrate.

5.0 g. of the chloride treated as described for the corresponding tetrammine compound. After concentration the compound was crystallised by the addition of acetone. Yield, 4.4 g. Recrystallised from aqueous acetone. Yield, 4.1 g. The compound which crystallised in clear

colourless quadrilateral plates with angles $\neq 90^\circ$, was readily soluble in water to give an alkaline solution (litmus). Over P_2O_5 , $1\frac{1}{2}H_2O$ are lost, the remaining $\frac{1}{2}H_2O$ being very strongly held.

Found (air-dry material): Pt, 49.6%; F, 9.5%; H_2O , 7.2%, 6.6% (loss over P_2O_5 , no further loss on heating two hours at $140^\circ C.$).

$[Pt\{C_2H_4(NH_2)_2\}_2]F_2 \cdot 2H_2O$ requires Pt, 50.1%; F, 9.8%; $2H_2O$, 9.3%; $1\frac{1}{2}H_2O$, 7.0%.

Analyses.

Platinum analyses were made by igniting 0.1 g. of material in a platinum crucible. Fluorine was determined by boiling 0.1 g. material with excess aqueous ammonia until the odour of ammonia was faint and then by the standard method of adding sodium carbonate and precipitating calcium carbonate and fluoride with calcium chloride. The separated material was ignited in a platinum crucible treated with excess acetic acid and evaporated to dryness on the water bath. The calcium fluoride was filtered, ignited and weighed. The calcium fluoride was converted to calcium sulphate as a check. Finally the calcium sulphate was dissolved in diluted hydrochloric acid and a small quantity of platinum (usually < 0.5 mg.) was filtered, ignited and weight deduced from calcium fluoride and calcium sulphate. Good agreement between calcium sulphate and calcium fluoride weight was obtained in each case. The fluoride percentage was not corrected for small solubility of calcium fluoride in the water used for washing the precipitate. It is estimated that in compounds with 20% and 10% F. the result would probably be low by 2% and 4% respectively.

SUMMARY.

The preparation of the fluorides and hydrogen fluorides of $[Pt(NH_3)_4]^{++}$, $[Pt(C_5H_5N)_4]^{++}$, and $[Pt\{C_2H_4(NH_2)_2\}_2]$ are described. They are all well defined, colourless crystalline compounds, readily soluble in water. Evidence was obtained that compounds with mixed fluoride and hydrogen fluoride anions exist.

ACKNOWLEDGEMENTS.

The author is indebted to Dr. P. F. J. Dwyer for initially suggesting this programme and for his interest and suggestions during the course of the work.

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PART IV

INVOLUTIONS ON A CONIC AND ORTHOGONAL MATRICES.

By F. CHONG, M.A., M.Sc.

(Communicated by PROFESSOR T. G. ROOM, F.R.S.)

Manuscript received, October 12, 1949. Read, December 7, 1949.

Let s be a given non-degenerate conic in a plane π . Each point P of π (P not on s) determines an involutory self-transformation P of s and every such transformation is determined by a point of π not on s . (The identity will not be regarded as an involution here.) If a line through P meets s in points U, V we shall write $UP=V$. If Q is any point of π and VQ meets s again in W , we write

$$UPQ=VQ=W.$$

It is clear that the operators P, Q, \dots form a multiplicative set which are fully associative; the product of any number of these operators is a projectivity which is not, in general, an involution. The involutory transformations of a conic form a subset, never a subgroup, of the group of transformations of the conic.

The aim of the first part of this paper is to discuss the conditions under which the product $A_1A_2 \dots A_{n-1}$ of a number of involutions is an involution A_n . This is equivalent to the conditions that

$$A_1A_2 \dots A_n=I \tag{1}$$

where I is the identical transformation.

The problem of inscribing a polygon $P_1P_2 \dots P_n$ in s so that P_iP_{i+1} passes through A_i (A_1, \dots, A_n being n given distinct points) is known to have two solutions in general. [See, e.g., Salmon, 1850.] The condition that this problem have an infinity of solutions is obviously that the relation (1) above should hold.

For the case $n=2$ we see at once that $A_1A_2=I$ if, and only if, $A_1=A_2$, i.e. $A_1=A_2$.

For $n=3$ we shall prove

Theorem 1. A necessary and sufficient condition that $A_1A_2A_3=I$ is that $A_1A_2A_3$ should be a self-polar triangle with respect to s .

Given that $A_1A_2A_3=I$, let A_1A_2 meet s in points U, V . So $UA_1A_2A_3=U$ and $UA_1A_2=U$; therefore $UA_3=U$. I.e. A_3 lies on the tangent at U .

Similarly, we see that A_3 must lie on the tangent at V ; and therefore A_3 is the pole of A_1A_2 .

Since $A_1A_2A_3=I$ and $A_3^2=I$ we have

$$A_3A_1A_2=I.$$

Therefore A_2 is the pole of A_3A_1 . Hence $A_1A_2A_3$ is a self-polar triangle.

The above proof breaks down if U and V coincide. In this case A_1, A_2, A_3 would have to be collinear on a tangent of s . It will be seen from Theorem 2 below that, if A_1, A_2, A_3 are collinear then $A_1A_2A_3$ is always an involution and therefore cannot be the identity. Thus U and V would never coincide.

Conversely, if $A_1A_2A_3$ is a self-polar triangle, take any point P on s and let $PA_1=Q$, $QA_2=R$, $RA_3=S$, $SA_2=P'$. If A_2A_3 meets A_1P and A_1S in A_1' and A_1'' respectively, then

$$(A_1A_1', PQ) = -1 = (A_1A_1'', RS).$$

Hence P and P' coincide and PR , QS must meet at A_3 . Therefore $RA_3=P$ and so

$$PA_1A_2A_3=P \text{ or } A_1A_2A_3=I.$$

Corollary 1. The necessary and sufficient condition that AB be an involution is that A, B be conjugate points with regard to s .

Corollary 2. If the product of A, B and C in any one order is the identity then it is so for every order. (This is also obvious algebraically.)

For the case $n=4$ we shall prove :

Theorem 2. A necessary and sufficient condition that $A_1A_2A_3A_4=I$ is that A_1, \dots, A_4 be collinear on a line l meeting s in U, V such that $(U, V), (A_1, A_3), (A_2, A_4)$ are pairs of an involution on l .

First, notice that if $PAB=P$ then A, B, P are collinear.

Given that $A_1 \dots A_4=I$, let A_1A_2 meet s in U, V . Then $UA_1A_2=U$ and $VA_1A_2=V$.

But $A_1A_2=A_4A_3$; therefore $UA_4A_3=U$ and $VA_4A_3=V$. So A_3 and A_4 must lie on UV ; i.e., A_1, \dots, A_4 are collinear. (The proof is still valid if U and V coincide.)

Now take any point P on s and let $PA_1=Q$, $QA_2=R$, $RA_3=S$. Therefore $SA_4=P$. Hence $(U, V), (A_1, A_3), (A_2, A_4)$ are pairs of an involution.

The converse result is easily proved.

Corollary. The product of three involutions ABC is an involution if, and only if, A, B, C are collinear.

Before treating the general value of n we shall require the following

Lemma A. Any projective transformation L of s into itself can be expressed as the product of two involutions and this can be done in ∞^1 ways.

For, let U, V be the self-corresponding points of the projectivity L and let $PL=Q$ where P is an arbitrarily chosen point of s . Take any point M on UV and let PM meet s again in R and RQ meet UV in N .

Now $PLNM=P$, and also

$$ULNM=U, VLNLM=V.$$

Thus U, V, P are three distinct self-corresponding points of the projectivity LNM which must therefore be the identity.

Hence $L=MN$.

M was chosen arbitrarily on UV and N was then uniquely determined; thus L is expressible as the product of two involutions in ∞^1 ways.

If the given projectivity is parabolic the theorem is still true but the above proof will need modification.

We now discuss our initial problem for a general value of $n(>4)$.

$A_1A_2 \dots A_{n-2}$, being a projectivity, is, by the above lemma, expressible as the product of two involutions MN . Moreover, if U, V are the self-corresponding points of this projectivity, then M, N lie on UV .

The condition that

$$A_1 A_2 \dots A_n = I$$

will therefore be the condition that

$$MNA_{n-1}A_n = I.$$

From Theorem 2 it follows that this is equivalent to the condition that A_{n-1} and A_n should lie in UV and that $(U, V), (M, A_{n-1}), (N, A_n)$ be pairs of points in involution.

Since $A_1 \dots A_{n-2} \neq I$ (we assume that $A_1 \dots A_n$ contains no superfluous factors) it follows that there exist just two polygons of $(n-2)$ sides inscribed in s with their sides passing through A_1, \dots, A_{n-2} in order, U being the first vertex of one polygon and V the first vertex of the other.

We have thus proved

Theorem 3. A necessary and sufficient condition that $ABC \dots PQ$ be an involution is that the point Q should lie on the line joining the self-corresponding points of the projectivity $ABC \dots P$.

The following deductions are immediate.

Corollary 1. The freedom of sets of points A_1, \dots, A_n such that $A_1 A_2 \dots A_n = I$ is $2n-3$.

Corollary 2. If $A_1 A_2 \dots A_n = I$ then the self-corresponding points of the transformation $A_{i+2} A_{i+3} \dots A_n A_1 \dots A_{i-1}$ are the intersections of $A_i A_{i+1}$ with s .

Corollary 3. If A, B, \dots, J, K be an odd number of points lying on a line l then $AB \dots K$ is an involution. (The self-corresponding points of $AB \dots J$ are the intersections of l with s .)

Algebraic Contents of the Results.

Taking the conic s in the form

$$x_0 : x_1 : x_2 = t_1^2 : t_0 t_1 : t_0^2$$

where (x_0, x_1, x_2) are homogeneous coordinates in the plane and (t_0, t_1) homogeneous parameters, the involutory self-transformation P of s determined by the point $P(p_0, p_1, p_2)$ may be expressed thus:

$$\begin{pmatrix} t_0 \\ t_1 \end{pmatrix} = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \begin{pmatrix} t_0^* \\ t_1^* \end{pmatrix}$$

where $p_0 p_2 - p_1^2 \neq 0$ since P does not lie on s . Writing

$$P = \begin{pmatrix} p_1 & -p_0 \\ p_2 & -p_1 \end{pmatrix} \quad (2)$$

we see that P is fully characterised by the (non-singular) matrix P which is called an involutory matrix. [$P^2 = (p_0 p_2 - p_1^2)I$.] In other words, a 2 by 2 matrix is involutory if, and only if, it is of the form (2).

The above theorems, obtained geometrically, yield at once the following algebraic results.

Theorem 4. The product of two involutory 2 by 2 matrices AB is an involutory matrix, if, and only if,

$$a_0 b_2 + a_2 b_0 - 2a_1 b_1 = 0,$$

where

$$A = \begin{pmatrix} a_1 & -a_0 \\ a_2 & -a_1 \end{pmatrix} \text{ etc.}$$

Theorem 5. The product of three 2 by 2 involutory matrices ABC is an involutory matrix if, and only if,

$$\begin{vmatrix} a_0 & a_1 & a_2 \\ b_0 & b_1 & b_2 \\ c_0 & c_1 & c_2 \end{vmatrix} = 0.$$

Theorem 6. Let A, B, \dots, J, K be a set of involutory 2 by 2 matrices and let $AB \dots J = R$ where R may, or may not, be involutory. If the eigen-vectors of R be (r_{01}, r_{11}) and (r_{02}, r_{12}) then a necessary and sufficient condition that $AB \dots JK$ be an involutory matrix is

$$\begin{vmatrix} r_{01}^2 & r_{01}r_{11} & r_{11}^2 \\ r_{02}^2 & r_{02}r_{12} & r_{12}^2 \\ k_0 & k_1 & k_2 \end{vmatrix} = 0,$$

where

$$K = \begin{pmatrix} k_1 & -k_0 \\ k_2 & -k_1 \end{pmatrix}$$

[An eigen-vector of an n by n matrix A is a non-zero vector x satisfying $Ax = \lambda x$ for an appropriate scalar λ . There are, in general, n independent eigen-vectors corresponding to the n values of λ given by $|\lambda I - A| = 0$.]

Theorem 3, Corollary 3, gives

Theorem 7. If A_1, \dots, A_n be an odd number of involutory 2 by 2 matrices, where

$$A_i = \begin{pmatrix} a_{1i} & -a_{0i} \\ a_{2i} & -a_{1i} \end{pmatrix},$$

then the relations

$$\begin{vmatrix} a_{01} & a_{02} & \dots & a_{0n} \\ a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \end{vmatrix} = 0$$

imply that the product $A_1 A_2 \dots A_n$ is an involutory matrix.

Corollary. If A and B are involutory then so are $(AB)^n A$ and $(AB)^n B$. This is also obvious algebraically and holds for square matrices of any order.

Relation to Orthogonal Matrices.

We now consider the relation of the above results to orthogonal matrices of order three. In the remainder of this paper all matrices denoted by capital letters are square matrices of the third order, all vectors are denoted by lower case letters and are regarded as 3 by 1 matrices, and the transpose of a matrix will be signified by a dash. For any vector such as a we shall assume that $a' = (a_1, a_2, a_3)$. Also, a point P of coordinates (p_1, p_2, p_3) shall be referred to as the point p or the point of coordinate vector p (i.e. using the corresponding lower case symbol).

If the conic s , used above, be taken in the plane π at infinity ($x_0 = 0$) with equation

$$x_1^2 + x_2^2 + x_3^2 = 0,$$

then any (non-singular) collineation of the plane π into itself which leaves s invariant is an orthogonal transformation; and the converse is true. Writing this collineation as

$$\rho x^* = Ax$$

then A may be taken as an orthogonal matrix. If A is real with determinant equal to $+1$ then this transformation corresponds to a proper rotation in ordinary cartesian space.

In the geometrical results above we were concerned exclusively with transformations of the points on the conic s . It is clear that any projectivity on s can be extended into a collineation of the whole plane π and, moreover, this extension is unique. For, if T and T^* are two such extensions then $T^{-1}T^*$ would leave every point of the non-degenerate conic s invariant. On examining the possible types of collineations in a plane corresponding to the six distinct Segre characteristics, [Todd, 1947] it follows that $T^{-1}T^*$ must be the identity; that is, $T=T^*$.

In particular the involution P on s corresponding to the point P extends (uniquely) into an involutory collineation of π , namely, the harmonic inversion in the point P and its polar p with respect to s . We shall refer to this as the involutory collineation P determined by the point P . This can be interpreted in ordinary cartesian space as a reflection of (unsensed) lines through the origin O in a plane through O .

The matrix of the involutory collineation P is easily found as follows. The polar of the point P , of coordinate vector p , with respect to the conic $x'Ax$, is $p'Ax=0$. Denoting the involutory collineation determined by P by

$$xx^*=Px,$$

we see that x and x^* must be of the form

$$x=\lambda p+q \text{ and } x^*=-\lambda p+q$$

where q is the point of intersection of the polar of P with the line joining P to x . Therefore

$$x^*=x-2\lambda p.$$

Since Q lies on the polar of P

$$p'A(x-\lambda p)=0,$$

giving

$$\lambda=(p'Ax)/p'Ap.$$

Hence

$$xx^*=\left(I-\frac{2pp'A}{p'Ap}\right)x,$$

and so P may be taken in the form

$$P=\rho\left(I-\frac{2pp'A}{p'Ap}\right).$$

Now the coordinate vectors of points not on s may be normalised to unit magnitude and the conic s may be taken as $x'x=0$. Then $A=I$, $p'p=1$ and we have P in the form (taking $\rho=-1$ to make $|P|=1$),

$$P=-I+2pp'. \quad (3)$$

P is symmetric, orthogonal and involutory (any two of these adjectives imply the third). Moreover, it is clear that every symmetric proper orthogonal matrix of the third order must be expressible in the form (3).

Theorem 1, Corollary 1, therefore yields

Theorem 8. The product of two symmetric orthogonal matrices P , Q is also symmetric and orthogonal if, and only if, $p'q=0$.

Interpreted in ordinary cartesian space this may be stated as follows:

The product of two reflections, in planes α , β , is a reflection if, and only if, α is perpendicular to β . (The reflections are of unsensed lines through the origin O in planes through O .)

Theorem 2 and its corollary also give

Theorem 9. The product of three symmetric orthogonal matrices A, B, C is also symmetric and orthogonal if, and only if, the scalar triple product $[a, b, c]$ vanishes. (It is assumed that each of the three matrices is expressed in the form (3) above.)

In ordinary cartesian space this can be stated as follows :

The product of three reflections A, B, C , in planes α, β, γ , respectively, is a reflection if, and only if, α, β, γ have a line in common.

Suppose this condition is satisfied and the product is a reflection D . In the plane π , the points A, B, C, D will lie on a line meeting s in U, V such that $(U, V), (A, C), (B, D)$ are in involution. Therefore

$$(UV, AB) = (VU, CD) = (UV, DC).$$

But $(UV, AB) = e^{2i\theta}$ where θ is the angle between the planes α and β . [See e.g. Baker, 1928, whose terminology we follow here.] That is, if β is obtained from α by rotation through an angle θ then δ is obtained from γ by rotation through $-\theta$.

Rotations. Any (non-singular) collineation R of the plane π which leaves s invariant induces a projectivity on s whose self-corresponding points are, say, U, V . Let us denote the line UV by l and the pole of l with respect to s by L . Since U and V are self-corresponding points of R , it follows that l is a self-corresponding line on which R induces a projectivity with U, V as the united points. The characteristic cross ratio of this projectivity is (UV, PP') where P is on l and $P' = PR$, and this cross ratio is independent of the choice of P on l . In cartesian space with origin O , the angle $POP' (= \theta, \text{ say})$ is given by

$$2i\theta = \log (UV, PP'),$$

and OL is normal to the plane Ol . It is therefore clear that the collineation R corresponds, in cartesian space, to a rotation about the vector l as axis through an angle θ .

The lemma A preceding Theorem 3 yields

Theorem 10. Any orthogonal matrix can be factorised into the product of two symmetric orthogonal matrices, each of the form $-I + 2pp'$, and this can be done in ∞^1 ways.

In ordinary cartesian space, we may say, with more detail :

Any rotation L , about an axis l through an angle ϕ , can be expressed as the product MN of two reflections, in planes μ, ν , respectively, say ; μ must be taken arbitrarily through l and ν is then uniquely determined. (Or, ν could be chosen arbitrarily and then μ is uniquely determined.)

We will show further, now, that the angle between μ and ν is $\frac{1}{2}\phi$.

Using the notation of Lemma A, let PN meet s in S and SQ meet UV in H . Therefore

$$L = MN = NH.$$

Now the pencil of conics through the points P, Q, R, S determine an involution on l in which $(M, N), (U, V)$ are pairs and N is a double point ; the other double point is G , the intersection of l with the polar of N . Therefore

$$ML = MMN = MN = H.$$

As M varies on l , the points M, N are in 1-1 correspondence in which U, V are the united points ; also $M \rightarrow N$ and $N \rightarrow H$. So

$$(UV, MN) = (UV, NH)$$

and hence

$$(UV, MH) = (UV, MN)^2.$$

It follows that the angle from μ to ν is $\frac{1}{2}\varphi$.

Theorem 3 now gives

Theorem 11. The product of reflections A, B, \dots, J, K (in planes $\alpha, \beta, \dots, \kappa$, say) is also a reflection if, and only if, the plane κ passes through the axis of the rotation defined by $AB \dots J$.

It should be noticed that this statement remains valid when $AB \dots J$ is a reflection if we call the normal to the plane defining the reflection its "axis".

A purely algebraic formulation of this result may be conveniently given in terms of real matrices. A real orthogonal matrix R , if it is not symmetric, has one, and only one, real eigen vector which we shall denote by the corresponding lower case letter r . Let A, B, \dots, J, K be a set of real, symmetric, orthogonal (and, therefore, also involutory) matrices; and also let $AB \dots J = R$ where R is not symmetric. Then a necessary and sufficient condition that $AB \dots JK$ be symmetric is $r'k=0$. If R is symmetric, but is not the identity, the above condition is still valid provided r is taken to be that eigen vector of R which is uniquely determined, i.e. r is the normal to the plane defining the reflection R . The case $R=I$ is trivial.

Vector Form for Rotations. The above results enable us to obtain vector forms for a rotation and for the composition of two rotations, the axis of a rotation being specified by a unit vector and the angle by a scalar.

Every real, proper, orthogonal matrix A is of the form e^Q where Q is skew-symmetric [Taber, 1892]. Suppose

$$Q = \begin{pmatrix} 0 & -q_3 & q_2 \\ q_3 & 0 & -q_1 \\ -q_2 & q_1 & 0 \end{pmatrix},$$

where the q_i are real numbers, not all zero. The characteristic equation of Q is

$$\lambda^3 + (q_1^2 + q_2^2 + q_3^2)\lambda = 0,$$

so that we have, by the Hamilton-Cayley theorem,

$$Q^3 = -q^2 Q,$$

where $q' = (q_1, q_2, q_3)$ and $q = |q|$.

Writing $Q = qS$, then

$$S = \begin{pmatrix} 0 & -s_3 & s_2 \\ s_3 & 0 & -s_1 \\ -s_2 & s_1 & 0 \end{pmatrix},$$

where $s_i = q_i/q$; thus the vector defined by $s' = (s_1, s_2, s_3)$ is a unit vector. We now have $S^3 = -S$ and therefore

$$\begin{aligned} A &= e^Q = e^{qS} \\ &= I + qS + \frac{q^2 S^2}{2!} - \frac{q^3 S}{3!} - \frac{q^4 S^2}{4!} + \dots \\ &= I + \sin qS + (1 - \cos q)S^2 \end{aligned} \quad (4)$$

Now $Ss = s \times s = O$ and therefore $S^2 s = O$.

Hence $As = s$ and it follows that s is the axis of the rotation A defined by A .

Let the angle of rotation of A be θ , so that A is fully and uniquely determined by s and θ . Regarding s , and therefore S , as fixed, we may write

$$f(\theta) = A = e^{qS} = I + \sin qS + (1 - \cos q)S^2 \quad (5)$$

where q is some function of θ . For any integer n we have

$$f(n\theta) = A^n = e^{nqS} = I + \sin nqS + (1 - \cos nq)S^2, \quad (6)$$

and, in fact, this holds for any rational number n . It can now be readily shown that $q \equiv \theta \pmod{2\pi}$. Therefore, the rotation has matrix

$$A = e^{\theta S} = I + \sin \theta S + (1 - \cos \theta) S^2,$$

and hence, for any vector \mathbf{x} ,

$$A\mathbf{x} = \mathbf{x} + \sin \theta \mathbf{s} \times \mathbf{x} + (1 - \cos \theta) \mathbf{s} \times (\mathbf{s} \times \mathbf{x}), \quad (7)$$

since $S\mathbf{x} = \mathbf{s} \times \mathbf{x}$ and $S^2\mathbf{x} = S(S\mathbf{x}) = \mathbf{s} \times (\mathbf{s} \times \mathbf{x})$.

Now let A, B be two rotations about axes \mathbf{a}, \mathbf{b} (unit vectors) through angles $2\theta, 2\varphi$, respectively. In the plane at infinity, let A, B be the points of coordinate vectors \mathbf{a}, \mathbf{b} , and let their polars, with respect to s , be λ, μ , respectively; also denote the point (λ, μ) by N ; N is therefore the pole of AB and we may take $\sin \gamma \mathbf{n} = \mathbf{a} \times \mathbf{b}$. By Theorem 10, there exists a point M on λ and a point L on μ such that

$$A = MN \text{ and } B = NL.$$

Hence $AB = ML$. Denoting the pole of ML by C (given by a unit vector \mathbf{c}) and the interval ML by ψ we see that AB is a rotation C about the axis \mathbf{c} through the angle 2ψ . It follows from Theorem 10 that $M \rightarrow N$ by a rotation about \mathbf{a} through angle θ , and so we have, using (7),

$$\begin{aligned} \mathbf{m} &= \mathbf{n} - \sin \theta \mathbf{a} \times \mathbf{n} + (1 - \cos \theta) \mathbf{a} \times (\mathbf{a} \times \mathbf{n}) \\ &= \cos \theta \mathbf{n} - \sin \theta \mathbf{a} \times \mathbf{n}. \end{aligned}$$

Similarly,

$$\mathbf{l} = \cos \varphi \mathbf{n} + \sin \varphi \mathbf{b} \times \mathbf{n}.$$

$$\begin{aligned} \text{Therefore } \cos \psi &= \mathbf{l} \cdot \mathbf{m} = \cos \theta \cos \varphi - \sin \theta \sin \varphi (\mathbf{a} \times \mathbf{n}) \cdot (\mathbf{b} \times \mathbf{n}) \\ &= \cos \theta \cos \varphi - \sin \theta \sin \varphi \cos \gamma. \end{aligned}$$

where $\cos \gamma = \mathbf{a} \cdot \mathbf{b}$, and so we have obtained an expression for the angle 2ψ of the resultant rotation C .

To find the axis of C we have

$$\begin{aligned} \mathbf{m} \times \mathbf{l} &= (\sin \theta \cos \varphi) \mathbf{a} + (\cos \theta \sin \varphi) \mathbf{b} - \sin \theta \sin \varphi (\mathbf{a} \times \mathbf{n}) \times (\mathbf{b} \times \mathbf{n}) \\ &= (\sin \theta \cos \varphi) \mathbf{a} + (\cos \theta \sin \varphi) \mathbf{b} - (\sin \theta \sin \varphi) \mathbf{a} \times \mathbf{b}. \end{aligned}$$

The axis \mathbf{c} of C is parallel to $\mathbf{m} \times \mathbf{l}$ and is therefore determined.

If we write $\mathbf{a}_1 = \tan \theta \mathbf{a}$, $\mathbf{b}_1 = \tan \varphi \mathbf{b}$ then \mathbf{c} is parallel to the vector $\mathbf{a}_1 + \mathbf{b}_1 - \mathbf{a}_1 \times \mathbf{b}_1$.

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NATURE AND OCCURRENCE OF PEAT AT HAZELBROOK, NEW SOUTH WALES.

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OCCURRENCE AND ORIGIN.

Small lenses of well-preserved peat occur at depths of 5 to 6 feet in sandy soil about one mile north-west of Hazelbrook in the Blue Mountains. The material is of considerable interest owing to its unusual mode of occurrence and origin, and its significance in relation to early stages of coalification.

High-humus soils are common on elevated country, between 2000 and 4000 feet above sea level in the Eastern Highlands of New South Wales, but true peat has not formed as climatic conditions were not suitable during late Tertiary and Pleistocene time. In the Southern Highlands of New South Wales peat is accumulating at isolated places above 6000 feet on the Kosciusko Plateau, but alpine conditions in that area are quite different from those in any other part of New South Wales. In view of this, the occurrence of true peat at Hazelbrook (1000 feet above sea level) was investigated with the object of explaining its presence where climatic conditions have not been suitable for normal peat-formation.

The peat occurs as irregular lenses, up to 1 inch in thickness and 3 feet in diameter, distributed sporadically at the base of about 6 feet of sandy soil which lies on soft, partly weathered Hawkesbury Sandstone (Triassic) in a relatively mature valley of late Tertiary or early Pleistocene age. The sandy soil becomes more compact as it passes downwards from the surface. It also contains pebbly layers and horizons of ferruginous concretions which are typical of the underlying and surrounding beds of Triassic sandstone. The sandstone contains an argillaceous cement and relatively deep weathering or softening is common on old surfaces from which sand and clay have not been washed away. The pebbly layers and horizons of ferruginous concretions, in the sandy soil above the peat, lie parallel to the bedding of the underlying sandstone rather than the surface. This strongly suggests that the soil represents weathered or softened sandstone rather than recently transported alluvium.

From the nature of occurrence, outlined above, it appears evident that the peat is embedded in weathered Triassic sandstone, which presents an unusual problem as the peat has suffered very little compression and, from its general nature and properties, it is certainly much younger than the sandstone. At all other places plant material embedded in the Hawkesbury Sandstone during deposition is now in the form of hard bright coal of bituminous rank.

A possible explanation of the origin of the peat is suggested by the behaviour of roots of contemporary plants growing in the sandy soil above the peat. The partly weathered sandstone immediately beneath the peat appears to be a harder bed which has resisted weathering more than the overlying material. Roots of contemporary plants have found their way down through the completely softened sandstone and some have penetrated the peat lenses, but they have not entered the partly weathered sandstone underlying the peat. This suggests that the peat may have been formed by roots penetrating to the partly weathered

sandstone bed and spreading out to form "root mats" over a long period of time. Root material first introduced into the weathered sandstone in this way could have been preserved as a result of anaerobic conditions prevailing beneath ground-water level. With time, more roots probably entered the small root mats to become preserved after death, and thus add to the bulk of organic material in the peat lenses. Such a process would explain the occurrence of Pleistocene peat in weathered Triassic sandstone, and also the preservation of plant material to form peat in an area where climatic conditions have not been suitable for preservation at the surface in the normal manner.

The mode of origin outlined above was suggested after geological examination of the occurrence, and it was evident that if the peat had been formed in that way it would not contain pollen, spores or those parts of plants which extend above the surface of the ground. If, however, it had been deposited at the surface and subsequently buried it would be certain to contain aerial plant remains. In view of this, samples of the peat were submitted to Mr. J. Waterhouse, Department of Botany, University of Sydney, for microscopical examination with the object of obtaining further evidence relating to the nature of the material and its origin. His conclusions were as follows:

"Macroscopically, there appear to be roots in various stages of disintegration ramifying throughout the material. It was difficult to section the peat for microscopic study as it did not respond favourably to the usual procedure of wax-embedding. However, sections which were obtained exhibited normal root structures and revealed among the débris bodies that appear to be vesicles and subtending hyphæ of vesicular-arbuscular mycorrhizal fungi which normally occur associated with roots of some plants. No pollen grains were observed. The examination would therefore suggest that the peat has not originated from surface material, but rather that it was formed by accumulation of root material."

The foregoing results support conclusions based on geological evidence that the peat represents an accumulation of root material at some depth beneath the surface where it was preserved under anaerobic conditions below ground-water level. It follows that the occurrence does not necessarily indicate the recent existence of climatic conditions normally required for the formation of peat.

NATURE AND PROPERTIES.

The peat consists of soft fibrous root fragments, up to 8 inches in length and about $\frac{1}{4}$ inch in diameter, set in a matrix of finely divided root material and a stiff structureless gel-like substance. As a whole the peat is firm and compact but can be easily cut with a knife, and it is of a somewhat springy or rubbery nature when pressed or bent by hand. When taken from the moist sandy soil in which it occurs, the peat can be preserved in its original condition by storing in a closed jar. It also retains its original condition if placed over water in a closed jar, but when actually immersed it takes up, or absorbs, large amounts of water and swells to several times its original volume. When air-dried, the peat shrinks to about one-half its volume and becomes hard and brittle, but if immersed in water it readily takes up moisture and returns to its original condition. This property indicates that it has not reached the state of maturity, with respect to development of colloidal or micelle structure, at which irreversible physical changes occur when water is removed by drying (Dulhunty, 1946 and 1949).

For the purpose of chemical analysis and determination of maximum inherent moisture the peat was separated by hand into three components: A, Large pieces of root material. B, That portion of the peat which consisted mainly of finely divided fibrous material and a small amount of gel-like substance. C, The gel-like substance with very little fibrous material: Ultimate and proximate analyses were carried out on the three components, and values for

maximum inherent moisture were determined by Controlled Vaporisation of Adherent Moisture (for details of process see Dulhunty, 1947). Results of analyses and moisture values, shown in Table I, indicate that components A and B are very similar with respect to carbon, hydrogen and moisture, but ash and volatiles are considerably lower in A. Component C is lower in carbon but somewhat higher in hydrogen and moisture than components A and B.

TABLE I.
Analytical Data and Moisture Properties of Components in Hazelbrook Peat.

| Peat Component. | Percentage Ash-free Dry Peat. | | | | Percentage Dry Peat. | |
|-----------------|-------------------------------|-----------|-------|---------------|----------------------------|------|
| | Carbon. | Hydrogen. | Vols. | Fixed Carbon. | Maximum Inherent Moisture. | Ash. |
| A | 53.10 | 5.22 | 66.7 | 33.3 | 40.31 | 2.74 |
| B | 54.08 | 5.62 | 78.1 | 21.9 | 40.12 | 8.90 |
| C | 47.3 | 5.88 | 76.1 | 23.9 | 56.00 | 6.80 |

Component A, large pieces of root material, would appear to be the precursor of vitrain in higher rank coal, whilst component B, consisting of more finely divided fibrous material together with some of the gel-like substance, would probably become a canneloid clarain if coalification were to continue to bituminous rank. The low carbon content and high moisture value of the structureless gel-like substance, component C, suggest that it is some form of humic degradation product derived by limited biological decay of the root material. This substance probably represents the peat-stage or precursor of a homogeneous structureless cannel-coal constituent with unusually low hydrogen content and volatile yield owing to the complete absence of spores, cuticle and resin, which normally characterise cannel derived from surface plant-material.

The carbon contents and volatile yields of components A and B indicate that the peat is very immature with respect to chemical rank as changes have advanced only a little beyond the average composition of wood which contains about 50% carbon and yields about 80% volatiles. The small change which has taken place is evidently associated with the biological processes of preliminary decay followed by preservation under more or less anaerobic conditions.

Relationships between maximum inherent moisture and rank or carbon content, for vitrains of all rank from peat to anthracite, were recently investigated (Dulhunty, 1948). It was shown that in the peat stage the woody precursors of vitrain, with 55% to 60% carbon, have moisture values of 30% to 50%. As rank increases moisture rises to between 70% and 120% at brown-coal rank (carbon about 70%), where it reaches a maximum in the carbon-moisture relationship. With further increase in rank, moisture then falls to less than 5% at the well-known minimum at high-rank bituminous stage. In the case of the woody constituents, components A and B, in the Hazelbrook peat, the moisture values of about 40% for 53% to 54% carbon are in keeping with the general relationship established for the woody constituents of peats formed in the normal manner. The relatively low moisture values of about 40% indicate that the woody constituents of the Hazelbrook peat are very immature with respect to physical rank as well as chemical rank, and it is probable that much of the original physical structure of cellulose and lignin still remains, and that only a

limited amount of the true gel, or colloidal structure, of higher-rank peats and brown coals has developed. The somewhat higher moisture value of 56% for the gel-like substance, with 47.3% carbon suggests that its physical rank is in advance of its chemical rank, and that practically all the original ultra-fine structures of the plant materials have been replaced by the colloidal structures which represent the first stages in the formation of the micelle structures in higher-rank coals. This accounts for the springy or rubbery nature of the peat.

When carbon content reaches about 60%, and maximum inherent moisture rises to between 60% and 70%, low-rank coals reach the stage at which irreversible physical changes occur on drying (Dulhunty, 1948). At this stage it is believed that the ultra-fine structure consists essentially of well-developed micelles, the majority of which are just touching with very small contact points. The Hazelbrook peat has not yet attained this rank-stage, with respect to either physical or chemical rank. It is probable that its ultra-fine structure, in addition to residues of the original cellulose and lignin structure, consists mainly of "primary units" (Bangham, 1943), which eventually segregate to form micelles, dispersed in a watery medium. This degree of colloidal development, with the absence of micelles touching at contact points, would explain the fact that the peat can be dried and resaturated without causing permanent change in its ultra-fine structure. Also the condition of component C, which appears to consist almost entirely of unsegregated primary units dispersed in a watery medium, would account for the fact that the peat takes up water and swells to several times its original volume if immersed after removal from its place of occurrence where it is confined under slight pressure from the weight of overlying sand.

In general, it appears that the Hazelbrook material is a true but immature peat in which plant constituents have been partly changed to humic products representing the first step in the building of the complex "coal molecule", and that the material is in the earliest stages of the process of physical development which eventually gives rise to the well-organised micelle structure of coal. It is believed that further study of the physical and organic chemistry of such peats may provide important data and contribute towards a better understanding of the mechanism by means of which plant material is changed to coal.

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In conclusion, the writer wishes to thank Mr. A. G. Bourne, of Hazelbrook, for drawing his attention to the occurrence of peat in the locality. It is also wished to acknowledge the assistance of Mr. J. Waterhouse in botanical examination of the peat; laboratory work by Misses Nora Hinder and Ruth Penrose; and facilities provided by the Commonwealth Research Grant to the University of Sydney.

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THE RESOLUTION OF THE TRIS o-PHENANTHROLINE NICKEL II ION.

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When excess of o-phenanthroline is added to a nickel salt solution, pink coloured compounds result which have been shown to have the constitution $\text{Ni(phenan)}_3\text{X}_2 \cdot n\text{H}_2\text{O}$ (Pfeiffer and Tappermann, 1933). These substances are analogous to the tris 2:2' dipyridyl compounds $\text{Ni(dipy)}_3\text{X}_2 \cdot n\text{H}_2\text{O}$ which are also pink and have been resolved into enantiomorphous forms (Morgan and Burstall, 1931). With two molecules of phenanthroline to one of nickel salt, blue compounds may be isolated (Pfeiffer and Tappermann, *loc. cit.*), of the composition $\text{Ni(phenan)}_2\text{X}_2 \cdot n\text{H}_2\text{O}$. Whether these compounds are the octahedral complexes $[\text{Ni(phenan)}_2\text{H}_2\text{O}]\text{X}_2 \cdot (n-2)\text{H}_2\text{O}$ or simply hydrated 4-covalent complexes is unknown, but analogy with the hexammine and tetrammine series of nickel compounds supports the latter interpretation.

In the present communication the resolution of the tris o-phenanthroline nickel ion is described and also experiments carried out in an effort to resolve the blue bis compounds. The resolution of the tris-phenanthroline nickel ion was achieved by the addition of an excess of potassium d-antimonyl tartrate to a solution of the complex chloride, when the d-tris o-phenanthroline nickel d-antimonyl tartrate separated as a highly insoluble crystalline precipitate. The optically active acid was eliminated by the addition of alkali, and the active nickel complex precipitated as the sparingly soluble perchlorate. The laevo form was obtained from the filtrate by precipitation with sodium perchlorate solution. The active perchlorates were purified by recrystallisation from warm aqueous acetone, the d,l perchlorate impurity separating as the least soluble fraction.

The optical forms were much more stable than the active forms of the tris 2:2' dipyridyl nickel ion. Thus, whilst Morgan and Burstall (*loc. cit.*) found that solutions of the active form of this substance racemised completely in $1\frac{1}{2}$ hours at 20°C ., the phenanthroline complexes had lost only 50% of the activity in 18 hours, and at the end of $73\frac{1}{2}$ hours still possessed a slight rotation. An unexpected observation was that the racemisation rate was reduced in the presence of sulphuric acid. This effect is being studied in detail in order to gain information of the mechanism of racemisation.

Like the corresponding ruthenium compound $\text{Ru(phenan)}_3(\text{ClO}_4)_3$, whose resolution has been described previously (Dwyer and Gyarfás, 1949), when examined in the wavelengths 589.0 and 546.1 m μ , the nickel compound showed a large abnormal rotatory dispersion. The absorption and rotatory dispersion curves will be described in a subsequent communication.

When the blue solutions containing the biso-phenanthroline complex were treated with potassium antimonyl tartrate, pale pink precipitates of the tris phenanthroline complex were obtained even when the ratio of nickel to the base was only 1:1.5, suggesting that the bis complex was in equilibrium with the tris complex



This observation was confirmed by the precipitation of $\text{Ni}(\text{phenan})_3(\text{ClO}_4)_2$ from blue solutions, which had been boiled to ensure that any of the tris compound, accidentally prepared by a local high concentration of phenanthroline during the preparation of the bis compound should be transformed. The ease of change of the bis complex to the tris obviates all possibility of resolution.

EXPERIMENTAL.

A 4 dm. tube was used for all measurements of rotation.

d-Tris o-Phenanthroline Nickel d Antimonyl Tartrate.

d,l Tris o-phenanthroline nickel chloride was prepared as described by Pfeiffer and Tappermann (*loc. cit.*), by the addition of finely divided o-phenanthroline monohydrate (3.0 g.) to a solution of nickel chloride hexahydrate (1.2 g.) in water (100 mls.). The mixture was stirred until the phenanthroline had dissolved completely, and to the resulting red solution was added slowly a solution of potassium antimonyl tartrate (4.8 g.—3 mols.) in water (30 mls.). On scratching the sides of the vessel, a pink crystalline precipitate was obtained. The solution was cooled rapidly from room temperature to approximately 5° C. in ice and filtered. The precipitate was washed with ice water and purified by solution in 0.1 N caustic soda (50 mls.) and after filtration, precipitated by the addition of acetic acid and a little potassium antimonyl tartrate. The pure substance crystallised in pale pink needles.

A 0.02% solution in N/100 sodium hydroxide gave $\alpha = +0.76^\circ$; whence $[\alpha]_D^{15} = +950^\circ$.

Found: N=6.45%; Sb=18.79%.

Calculated for $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3]_2[\text{SbO}_3\text{C}_4\text{H}_4\text{O}_6]_2 \cdot 2.7\text{H}_2\text{O}$: N=6.49%; Sb=18.79%.

d,l-Tris o-Phenanthroline Nickel Perchlorate Dihydrate.

The inactive perchlorate prepared by the addition of sodium perchlorate solution to a solution of the inactive chloride gave pink rectangular prisms from hot aqueous acetone. The compound was very sparingly soluble in water.

Found: Ni=7.040%.

Calculated for $[\text{Ni}(\text{CH}_5\text{N}_2)_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: Ni=7.036%.

d-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.

The d tris o-phenanthroline nickel d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 mls.) by shaking at room temperature and the solution filtered. Sodium perchlorate solution was then added drop by drop, with scratching of the sides of the vessel when the d- perchlorate precipitated in pale pink micro crystals. After washing with ice water, the precipitate was dissolved in warm 30% acetone in water, and fractionally precipitated with sodium perchlorate. The first fraction was discarded and the more soluble fractions combined and recrystallised from aqueous acetone by the addition of sodium perchlorate. The substance crystallised in flat pink plates and was appreciably soluble in cold water to give a pink solution. A 0.02% solution in water gave $\alpha_D = +1.17^\circ$ and $\alpha_{5461} = +1.39^\circ$, whence $[\alpha]_D^{15} = +1463^\circ$ and $[\alpha]_{5461}^{15} = +1738^\circ$; or $[M]_D^{15} = +12,470^\circ$ and $[M]_{5461}^{15} = +14,810^\circ$.

Found: Ni=6.85%; N=9.25%.

Calculated for $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$: Ni=6.89%; N=9.23%.

l-Tris o-Phenanthroline Nickel Perchlorate Trihydrate.

The residual solution after the precipitation with potassium antimonyl tartrate was strongly laevo rotatory and was treated carefully with sodium perchlorate solution, avoiding an excess to prevent the precipitation of potassium perchlorate. Alternatively it was treated with sodium iodide solution and the insoluble iodide dissolved in aqueous acetone and then precipitated as the perchlorate. The perchlorate precipitate was recrystallised as for the d form above, and gave flat pink plates of the pure laevo perchlorate. Occasionally this substance appeared in a yellow

dimorphous form if the aqueous acetone solution was too hot. The yellow form gave a pink solution in water and had the same rotation as the pink form.

A 0.02% solution in water gave $\alpha_D = -1.17^\circ$ and $\alpha_{5461} = -1.39^\circ$, whence $[\alpha]_D^{15} = -1463^\circ$ and $[\alpha]_{5461}^{15} = -1738^\circ$; or $[M]_D^{15} = -12,470^\circ$ and $[M]_{5461}^{15} = -14,810^\circ$.

Found: Ni=6.89%; N=9.21%.

Calculated for $[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$: Ni=6.89%; N=9.23%.

SUMMARY.

Tris o-phenanthroline nickel perchlorate has been resolved through the antimonyl tartrate. The optical forms were much more stable than those of the tris 2:2' dipyridyl nickel ion, and showed a large abnormal rotatory dispersion.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for microanalyses (N), and one of us (E.C.G.) is indebted to the Commonwealth Research Committee for an Assistantship.

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A NOTE ON THE REACTION BETWEEN CHROMIUM II SALTS AND o-PHENANTHROLINE.

By F. P. DWYER, D.Sc.,
and H. WOOLDRIDGE, B.Sc.

Manuscript received, October 13, 1949. Read, December 7, 1949.

Edmonds, Hammett and Chapman (1934) by the reaction between chromous acetate and o-phenanthroline obtained a red solution, which was oxidisable to a purplish red colour. The potential of the reaction, which was reversible, was found to be approximately +0.77 volt, but because of the poor colour intensity and the unsuitable colour change the substance was considered valueless as a redox indicator. The original reddish coloured solution was claimed to contain tris o-phenanthroline chromium II acetate and the oxidation reaction to be



The substance responsible for the colour was not isolated and no analyses are available. The present note deals with attempts to isolate tris o-phenanthroline chromium II salts with a view to their systematic investigation and possible resolution.

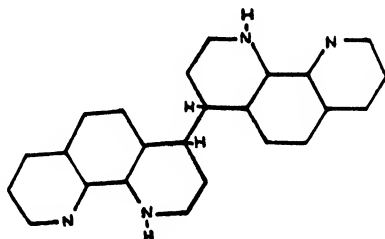
Chromous acetate, or better, chromous chloride or sulphate, was found to react with phenanthroline with the production of reddish solutions, which yielded orange amorphous precipitates with chloride or sulphate ion. The filtrates from the precipitations were still coloured and gave reddish crystalline precipitates with iodides and perchlorates. The amorphous precipitates were oxidisable with ceric and dichromate to the purple coloured solutions, but the red crystalline iodides and perchlorates were not.

The orange amorphous precipitates were nearly insoluble in water and the usual organic solvents, but dissolved easily in dilute acids on warming and reprecipitated in the amorphous condition on cooling or dilution. As originally prepared, the amorphous substances contained C, H, N, S and Cr, but after purification by repeated solution in acid and reprecipitation the chromium was lost but the substances, now an orange yellow colour, were still oxidisable with potassium dichromate to a purple colour which was destroyed reversibly by reducing agents.

The red crystalline iodides and perchlorates also contained organic matter and chromium, but were not oxidisable and appeared to be impure compounds of chromium III and phenanthroline. These substances which are the chromium analogues of the ferric phenanthroline compounds, $[\text{Fe(phenan)}_2\text{OH}]_2\text{X}_4$ (Gaines, Hammett and Walden, 1936), will be described in a subsequent communication.

It thus appears that the reaction between phenanthroline and chromium II salts yields a mixture of products, and the oxidisable substance is not a chromium II compound but a reduction product of o-phenanthroline. This observation was confirmed by reducing o-phenanthroline by a variety of methods in the absence of chromium salts. The reducing agents included zinc and hydrochloric acid, zinc-amalgam and sulphuric acid, sodium amalgam, sodium in alcohol, at a mercury surface polarographically and cathodically with a lead electrode. Cathodic reduction appeared the best method of obtaining the

reduction products free from metallic impurities. The reduced solutions were orange to orange red in colour and were reversibly oxidisable. They contained at least two substances, one of which was oxidisable and the other not. One of these substances isolated as the iodide was pale yellow, non-oxidisable and had the formula $C_{11}H_9N_2 \cdot HI$. A possible structure is



This substance appears to be the first product of reduction of phenanthroline, further reduction leading to the oxidisable material which has not been isolated pure.

Preliminary experiments on the reduction of o-phenanthroline polarographically (Breyer, Buchanan and Casimir, 1948) indicate that two steps are involved, the first of one electron and the second of three.

EXPERIMENTAL.

The Reaction between Chromium II Salts and o-Phenanthroline.

Chromium III chloride hexahydrate was reduced in hydrochloric acid solution with zinc amalgam until a blue colour resulted. Solid sodium acetate was added and the red crystalline chromium II acetate was filtered in an atmosphere of carbon dioxide. The solid acetate was added directly to oxygen-free solutions of o-phenanthroline acetate, or alternatively dissolved in 0.5 N sulphuric or hydrochloric acids and added to solutions of the base in aqueous alcohol. In all experiments red solutions resulted which yielded orange precipitates with chloride, sulphate, iodide or perchlorate.

All of the precipitates were reversibly oxidisable with potassium dichromate, or permanganate, bromine water and ceric salts.

With chromous sulphate good yields of the orange substance were obtained by the subsequent addition of sodium sulphate. After washing and drying the substance gave: C=43.84%; H=3.84%; N=7.93%; Cr=7.73%; (S not estimated); and after solution in sulphuric acid and reprecipitation with water: C=56.06%; H=4.98%; N=9.50%; Cr=2.03. With further purification the chromium was finally eliminated. The analytical figures did not agree with any possible compound, and it was concluded that the substance was an inseparable mixture.

The Cathodic Reduction of o-Phenanthroline.

The base 0.5 g. in sulphuric acid (50 cc., 1 N) was reduced at a lead cathode in a small beaker separated from the anode by the membrane of a sintered glass crucible. Current density = 0.02 amp./sq. dm.; time = 3 hours. The solution became pale orange and was finally evaporated to half its volume. After filtration from a small amount of orange precipitate, potassium iodide was added. The reddish precipitate was crystallised from hot water, leaving a red material insoluble, and gave large translucent yellow crystals, m.p. 200–202° C. This substance was not oxidisable.

Found: C=46.23%; H=3.38%; N=8.63%; I=41.0%.

Calculated for $C_{11}H_9N_2 \cdot HI$: C=46.46%; H=3.55%; N=9.03%; I=40.94%.

With longer reduction the solutions became orange red, and gave precipitates with iodides and perchlorates which were oxidisable. A base could be liberated with sodium carbonate. This substance melted above 300° C., and was highly insoluble except in acids. Despite many attempts analytically pure specimens could not be isolated and the structure of the oxidisable substance is still unknown.

The Potentiometric Oxidation of the Reduction Product.

The material for these measurements was made by reduction with chromous salts or cathodically. The curves obtained, which showed only one break, were identical and within the limits of experimental error gave the same value for the redox potential.

The reaction was carried out at 0° C. to increase the stability of the oxidised product and the measurements were made as quickly as possible. The titrating agent was ceric sulphate, the electrode smooth platinum foil, and the redox potentials shown in Table I were estimated from the half titration value.

TABLE I.

| Acid Concentration. | Potential. (Volts.) |
|----------------------------------|------------------------|
| H ₂ SO ₄ . | |
| 10 N | 0.90 |
| 7 N | 0.88 |
| 5 N | 0.87 |
| 3 N | 0.86 |
| 2 N | 0.86 |

On standing the purple colour was gradually discharged, but could be regenerated by the addition of more of the oxidising agent.

SUMMARY.

The reaction between chromium II salts and o-phenanthroline has been found to yield not complex chromium II compounds but a mixture of orange reduction products, one of which can be oxidised to a purple substance. The reduction could also be effected cathodically and by strong reducing agents such as zinc and acid. One of the reduction products isolated as the hydriodide had the formula C₁₂H₈N₂.HI, but was not oxidisable. The redox potential of the oxidisable material was approximately +0.87 volt.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for microanalyses and Miss E. C. Gyarmas for assistance with the potentiometric titrations.

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DETERMINATION OF THE BOILING POINTS OF AQUEOUS NITRIC ACID.

By L. M. SIMMONS, B.Sc., Ph.D., F.A.C.I., A.R.I.C.,
and MARTIN J. CANNY.*

With two text-figures and three tables.

Manuscript received, October 5, 1949. Read, December 7, 1949.

Inconsistencies in the published boiling points of aqueous hydrogen chloride solutions led to the design of a static method for rapidly determining the boiling points of pure and mixed liquids which do not attack mercury, glass or tap lubricant (Simmons, 1945). The method was later developed to eliminate the tap lubricant (Simmons, 1947), and the present further adaptation described herein enables the method to be used with liquids which attack mercury, such as aqueous nitric acid.

As was the case for aqueous hydrogen chloride solutions, the boiling points of aqueous nitric acid have hitherto been determined by dynamic methods, and these are known to suffer from two important sources of error, viz. superheating and change in concentration during the distillation of all samples except the azeotropic solution. The boiling points of aqueous nitric acid given in the International Critical Tables are based on the observations of Creighton and Githens (1915) using a dynamic method due to Young (1902). Although Young claimed that with the large quantity of liquid present and the small flame that is required, there is no fear of the vapour being superheated, he later stated in his monograph (1922) that "the boiling point of a liquid can only be correctly determined by observing the temperature of the liquid itself under such conditions that ebullition is impossible". This latter view is in accord with the conclusion arrived at by Swietoslowski (1945).

Table I shows the values published at various times for the boiling point and composition of the constant boiling mixture of water and nitric acid at or near standard pressure.

TABLE I.
Boiling Point and Composition of Constant Boiling Aqueous Nitric Acid.

| Date. | Observed by. | Pressure. (Millimetres Mercury.) | B.p. (° C.) | Percentage HNO ₃ by Weight. | Remarks. |
|----------------|---------------------------|--|-----------------|--|-----------------------------------|
| Before 1861 | Dalton <i>et al.</i> | Not stated | 120 | 66-70 | Reported by Roscoe, 1861. |
| 1861 | Roscoe. | 735 | 120.5 | 68.0 | |
| 1915 | Creighton and Githens. | 760 | 121.7- 121.8 | 68.18- 69.24 | |
| 1928 | — | 760 | 121.9 | 67.3 | International Critical Tables. |
| 1949 | Simmons and Canny. | 760 ± 0.5 | 120.6 ± 0.2 | 67.5 ± 0.5 | Present investigation. |

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RESULTS.

The boiling points found for aqueous nitric acid solutions at 760 mm. by the present method are shown by curve A (Fig. 1).

That portion of curve A which represents solutions containing more than 78 per cent. by weight of HNO_3 is dotted in order to indicate that decomposition

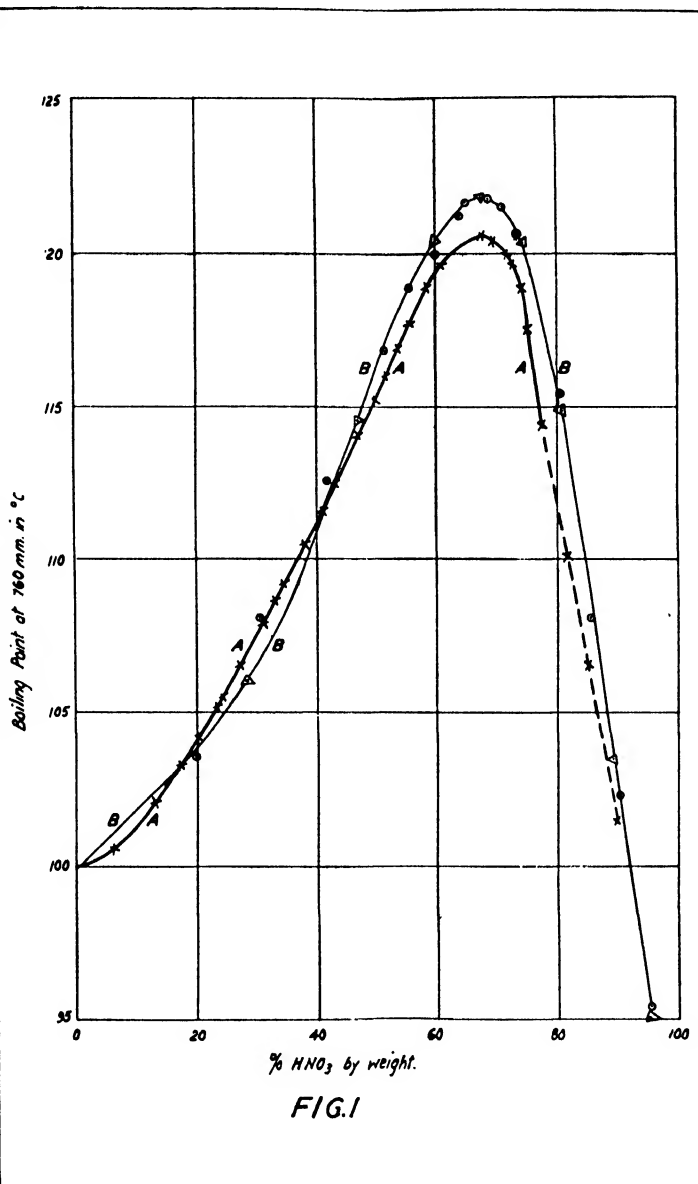


Fig. 1.—The Boiling Points of Aqueous Nitric Acid.

- A. According to the present investigation, observations plotted thus: X.
 B. According to the International Critical Tables. Tabulated values plotted thus: Δ.
 Creighton and Githens' observations plotted thus: ⊙.

takes place before the normal boiling points are reached. In such circumstances a normal boiling point cannot strictly be quoted, for the apparent boiling point would be affected by the rate of heating, the presence of light and of catalysts, and by other factors which may affect the rate of decomposition.

The data from which curve A was plotted is given in Table II.

TABLE II.

The Boiling Points of Aqueous Nitric Acid Containing Various Percentages by Weight of HNO₃ at a Pressure of 760 mm.

| Percentage HNO ₃ by Weight. | B.p. (° C.) | Percentage HNO ₃ by Weight. | B.p. (° C.) | Percentage HNO ₃ by Weight. | B.p. (° C.) |
|--|----------------|--|----------------|--|----------------|
| 0.0 | 100.0 | 37.9 | 110.5 | 69.2 | 120.4 |
| 6.1 | 100.6 | 41.0 | 111.7 | 71.7 | 120.0 |
| 12.9 | 102.1 | 43.0 | 112.5 | 72.2 | 119.7 |
| 17.0 | 103.3 | 47.3 | 114.1 | 73.7 | 118.9 |
| 20.3 | 104.2 | 49.7 | 115.2 | 75.3 | 117.6 |
| 23.3 | 105.2 | 52.0 | 116.0 | 77.4 | 114.4 d. |
| 24.0 | 105.6 | 53.6 | 117.0 | 82.1 | 110.1 d. |
| 27.2 | 106.6 | 56.0 | 117.7 | 85.6 | 106.6 d. |
| 31.0 | 107.9 | 58.5 | 118.9 | 89.6 | 101.5 d. |
| 32.7 | 108.7 | 62.0 | 119.6 | | |
| 34.5 | 109.2 | 67.5 | 120.6 | | |

d means that the sample decomposed at its boiling point.

For the purpose of comparison, Fig. 1 also shows a curve B, drawn according to the data given in the International Critical Tables. On this curve points marked \triangle indicate the International Critical Tables data, while points marked \odot show the observations listed by Creighton and Githens.

It will be seen that the boiling point of the constant boiling mixture is listed by the International Critical Tables as more than a centigrade degree higher than that found by the present method. It is of interest to recall that the same tables quote a maximum boiling point for hydrochloric acid more than a centigrade degree higher than that found by Simmons (1945) in confirmation of the measurements made by Bonner and Wallace (1930).

Table III is therefore submitted to replace that given on page 309 of Volume 3 of the First Edition of the International Critical Tables.

TABLE III.

| B = HNO ₃ . | | |
|------------------------|--------|--|
| B.p. (° C.) | M % B. | |
| 760 mm. | | |
| 100.0 | 0 | |
| 106.9 | 10 | |
| 113.9 | 20 | |
| 119.2 | 30 | |
| 120.6 | 37.2 | |
| 118.7 | 45 | |
| 111.3 | 55 | |
| 105.2 | 65 | |
| 102.2 | 70 | |

The last three entries in Table III refer to temperatures at which decomposition accompanies boiling.

APPARATUS AND PROCEDURE.

The J-tube shown in Fig. 2 is made of soda-glass and has an internal bore of about 7 mm. The length of the longer limb is about 20 cm. ; that of the

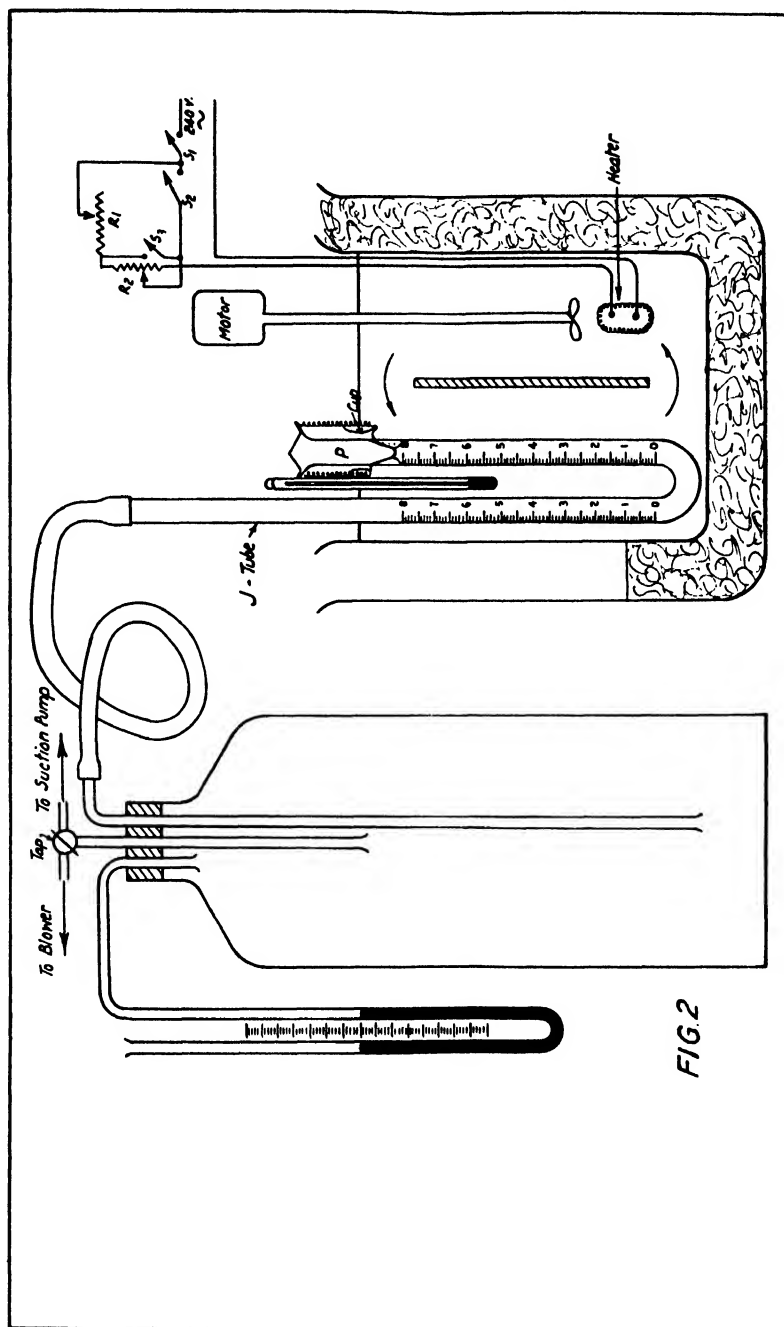


Fig. 2.—Boiling Point Apparatus.

shorter, including the stopper P, is about 14 cm. The stopper P is ground to a good fit in the socket at the top of the shorter limb and is surrounded by a cup

to retain a liquid seal. The stopper is held in place by spring ties. Both limbs are graduated in mm. from a datum line perpendicular to the axes of the limbs near the bend to a similar line just below the socket.

The heating bath consists of a large beaker containing paraffin B.P. or other high boiling transparent liquid. The beaker is well lagged except for the top and for an observation window in the side. In the beaker is supported a glass plate which touches the sides but whose upper and lower edges are about 2 cm. respectively below the liquid surface and above the bottom of the beaker. The motor-driven propeller causes the liquid to circulate rapidly as indicated by the arrows in Fig. 2.

The heater has a resistance of about 80 ohms. Switches S_1 , S_2 and S_3 , and the variable resistors R_1 and R_2 , enable the temperature of the bath to be raised or lowered rapidly or slowly at will.

The clean and dry J-tube, without the stopper, was clamped upright and into the shorter limb was poured enough of the nitric acid solution to reach a little more than half way up the millimetre scales. The tube was then placed in the heating bath so that the bath liquid reached about half-way up the side of the liquid seal cup when the propeller was in motion. The temperature of the bath was then rapidly raised by closing S_1 and S_2 until it was about 3°C . below the expected boiling point of the nitric acid solution. S_2 was then opened and closed judiciously until the solution had boiled gently for a few seconds in order to out-gas it. The J-tube was then removed from the bath and switches S_1 and S_2 were opened.

The rubber tube from the Winchester air bottle was then slipped over the open end of the longer limb and slight air pressure was applied by manipulating the tap until the solution in the J-tube rose to partly fill the liquid seal cup; the meniscus in the longer limb was then near the bend in the tube. The stopper P was inserted in its socket and held in place by the spring ties. That portion of the solution which was trapped in the cup provided a liquid seal.

By this time the temperature of the bath had fallen well below the boiling point of the solution, and the J-tube was replaced in the bath, a plumb-line being used to ensure verticality of the limbs. Switches S_1 and S_3 were closed, and R_1 was adjusted so that the bath temperature rose about $\frac{1}{4}^\circ\text{C}$. per minute; R_1 was found to be about 170 ohms.

The barometer was then read and corrected for temperature and gravity. Using this corrected reading, the pressure in the Winchester air bottle was adjusted by manipulating the tap until the mercury manometer indicated that the total pressure in the bottle was 760 ± 0.5 mm.

A short-stem thermometer, graduated in fifths of centigrade degrees, was clamped in the bath near the closed limb so that the graduation representing the expected boiling point was visible beneath the surface of the bath liquid through the inspection window.

As the temperature neared the boiling point of the solution, a vapour bubble formed beneath the stopper, and the solution was depressed in the shorter and raised in the longer limb. S_3 was then opened and R_2 adjusted so that the temperature fell about $\frac{1}{4}^\circ\text{C}$. per minute; R_2 was then found to be about 50 ohms. By opening and closing S_3 the temperature was adjusted until the menisci in the two limbs were at the same level. A final adjustment of the pressure in the bottle was made to ensure that it was 760 mm., and, if necessary, the bath temperature was altered slightly to compensate for this change in pressure. When the pressure in the bottle was within $\frac{1}{2}$ mm. of 760 mm., and the levels of the solution in the two limbs differed by not more than 2 mm., the thermometer was read to the nearest 0.1°C . By manipulating S_3 the temperature was

maintained nearly constant for five minutes, after which the pressure and temperature were again adjusted as above, and the temperature was again read. The J-tube was then removed from the bath, the rubber tube removed from the longer limb, and when the tube had cooled to ambient temperature, the solution was examined to see whether any uncondensed bubbles persisted beneath the stopper.

It was found that solutions containing more than 78 per cent. by weight of HNO_3 decomposed and turned brown on heating as described above. The decomposition progressed while the temperature was maintained at a constant value, so that in order to keep the menisci of these solutions at the same level, it was necessary to increase the pressure in the air bottle. When the J-tube was subsequently cooled to room temperature, a large bubble of gas remained uncondensed beneath the stopper. The lowest concentration at which this decomposition was detected was at 77.4% HNO_3 by weight, and the decomposition became increasingly apparent at higher concentrations.

Standardization of the Thermometer. The thermometer was tested by the Standards Laboratory, Sydney, over the range 90°C. to 130°C. for total immersion to an accuracy of $\pm 0.2^\circ\text{C.}$, and the reported corrections were applied to the readings.

Preparation of Aqueous Solutions of Nitric Acid. Solutions containing less than 70.2 per cent. HNO_3 by weight were prepared by mixing weighed quantities of "Analar" concentrated nitric acid and distilled water. More concentrated solutions were prepared by mixing the "Analar" acid with a 98.5 per cent. nitric acid prepared as follows.

Equal volumes of "Analar" concentrated nitric acid and concentrated sulphuric acid were mixed and distilled at a pressure of about 10 cm. of mercury in an all-glass still. The resulting distillate was mixed with an equal volume of concentrated sulphuric acid and again distilled at about 10 cm. Hg.

The azeotropic solution was prepared by mixing weighed quantities of "Analar" acid and water to yield a 68 per cent. solution of HNO_3 , and this was distilled at 760 mm. The first four-fifths of the distillate was rejected. The fact that the remainder of the distillate was truly the azeotropic mixture was assured by comparing its boiling point with the boiling points of mixtures of it with small quantities of concentrated acid and water respectively.

The concentrations of all solutions were determined by titration against sodium carbonate solution, using screened methyl orange indicator.

SUMMARY.

A method has been devised for the rapid determination of the boiling points of pure liquids and liquid mixtures which do not attack glass. The method obviates recourse to calculated corrections for emergent column and variations in atmospheric pressure, requires about 5 ml. of liquid, prevents sensible variations in composition of the liquid phase and avoids superheating. The method has been used to correct the list of boiling points of aqueous nitric acid appearing in the International Critical Tables. Solutions containing more than 78 per cent. HNO_3 by weight are found to decompose at or before reaching their boiling points. The constant boiling solution of nitric acid in water at 760 mm. is found to contain 67.5 ± 0.5 per cent. by weight HNO_3 and to have a boiling point of $120.6 \pm 0.2^\circ\text{C.}$ at 760 mm.

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REDUCTION BY DISSOLVING METALS.

PART VIII. SOME EFFECTS OF STRUCTURE ON THE COURSE OF REDUCTIVE FISSION.

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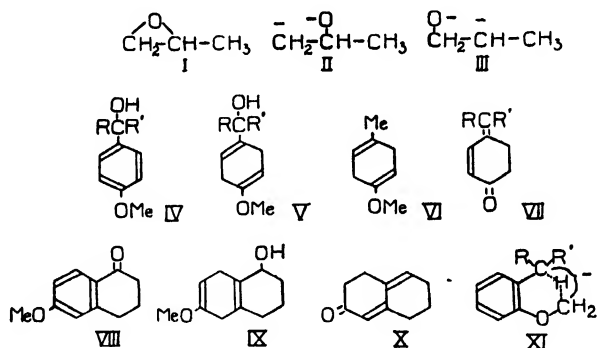
From an examination of the course of reductive fission by sodium-liquid ammonia solutions of diaryl ethers (Sowa *et al.*, 1937, 1938) and of aryl-alkyl ethers (Birch, 1947*a*) it has been concluded that the reactions proceed through transition states containing two anions: $R-O-R' + 2e \rightarrow (R^- + R'-O^-)$ or $(R'^- + R-O^-)$; the chosen transition state being the one of lower energy. By far the greater part of the energy is required to produce the carbon anions R^- or R'^- , that needed for $R-O^-$ or $R'-O^-$ being negligible by comparison (ROH , $pK \approx 18$, is a much stronger acid than RH , $pK \approx 37$). In practice it seems to be possible to neglect all other factors, e.g. differences in bond-strengths, and to compare the energies of the transition states on the basis of the energies of these carbon anions. The relations between structure and acidity (Birch, 1947*b*) lead to the conclusion that the greater the number of electron-repelling groups, such as alkyl, attached to a negatively charged carbon in a molecule, the greater will be its energy. Reduction should therefore proceed to give the least alkylated R-group as R^- .

This conclusion has been experimentally confirmed for aromatic systems (Birch, 1945, 1947*b*), which reduce because of resonance stabilisation of the anions, but has not been tested directly for saturated systems because they do not reduce. A confirmation of the theory in a similar case has now, however, been obtained by reducing 1 : 2-epoxypropane (I) to isopropyl alcohol. In this case the high ring-strain of the ethylene-oxide ring assists its reductive fission by contributing to the energy of the transition state (II). The same reduction can be carried out by sodium amalgam (Linnemann, 1866). That (II) should be formed rather than (III) can be predicted, because it contains CH_2^- , of lower energy than CH^- . The reaction cannot proceed by preliminary isomerisation to acetone, since acetone is largely unreduced under the conditions employed owing to the formation of its sodium salt.

The effect of a substituent in a benzene ring on the fission of aryl ethers (Sowa *et al.*, 1937, 1938; Birch, 1947*a*) is usually that to be expected from its known electronic character. The one outstanding exception so far examined is the methoxyl-group, whose influence depends on its position relative to the charged carbon atom formed in the process. In the *para*-position it shows the charge-destabilising effect to be expected from its normal electron-repelling character, but in the *ortho*-position it is charge-stabilising. In view of this unexpected dual behaviour, another reduction of a similar type, that of methoxy-phenylcarbinols, has been examined. The results confirm the orientation effects already observed: the *ortho*- and *meta*-methoxy-derivatives undergo reductive fission with loss of the hydroxyl-group, just as do the unsubstituted carbinols (Birch, 1945), e.g. 2- and 3-methoxyphenyl-carbinol give 2- and 3-isopropylanisole, but the *para*-methoxy-derivatives preponderantly retain the hydroxyl-group and reduce instead in the benzene ring. Small amounts of the fission

products are also obtained, but the only case where the amount is considerable is 4-methoxyphenylcarbinol (anisyl alcohol) (IV; R, R'=H), where it is clear from work already done (Birch, 1945) that the nuclear reduced compound (V; R, R'=H) can itself undergo reductive fission to the experimentally obtained 4-methyl-2:5-dihydroanisole (VI). The orientation of the two hydrogen atoms added to the benzene ring of the carbinol follows from the rule enunciated (Birch, 1944) and is confirmed by acid hydrolysis of the enol-ether group to a carbonyl. This hydrolysis is accompanied by dehydration to give the interesting diene-ketones (VII; R, R'=H or Me).

Anisyl alcohol produces a mixture of 4-methoxy-2:5-dihydrophenylcarbinol (V; R=R'=H), hydrolysed by acid to 4-methylenecyclohex-2-enone (VII; R=R'=H), and 4-methyl-2:5-dihydroanisole (VI). 4-Methoxyphenylmethylcarbinol (IV; R=H, R'=Me) gives chiefly 4-methoxy-2:5-dihydrophenylmethylcarbinol (V; R=H, R'=Me) hydrolysed to 4-ethylidenecyclohex-2-enone (VII; R=H, R'=Me), λ_{\max} 2,850 Å. Similarly, 4-methoxyphenyldimethylcarbinol (IV; R=R'=Me) gives 4-methoxy-2:5-dihydrophenyldimethylcarbinol, hydrolysed to 4-isopropylidenecyclohex-2-enone (VII; R=R'=Me). A particularly interesting case is the reduction of 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (VIII) to give 1-hydroxy-6-methoxy-1:2:3:4:5:8-hexahydronaphthalene (IX), hydrolysed by acid to 3-keto-1:2:3:5:6:7-hexahydronaphthalene (X). The light absorption of the last compound at λ_{\max} 2,900 Å. is in accord with its structure as a conjugated diene-ketone.



In all these cases, the transition state of reductive fission, e.g. $(4-\text{MeOC}_6\text{H}_4\text{CRR}' + \text{OH}^-)$ evidently requires so high an energy because of the influence of the *para*-methoxyl that the benzene ring is reduced for preference. That normal reductive fission occurs with the *meta*-methoxy compound is not astonishing, since the effect of a group in a *meta*-position is small, but the behaviour of the *ortho*-compound requires some explanation. One possible reason is that the methoxyl-group has a dual electronic character: an electron-attracting character due to the higher nuclear charge on the oxygen, and an electron-repelling character due to the unshared electrons of the oxygen atom. It is the latter which is usually more effective, especially if the group is attached to a polarisable system. There seems no reason, however, to expect one effect to operate for an *ortho*-group and the other for a *para*-group. A more likely explanation is that the *ortho*-negative charge is stabilised by cyclic hyperconjugation, which partly transfers it to the carbon of the methoxyl-group (XI). If this explanation is correct, no stabilisation should be observed with *tert*-butyl ethers lacking the necessary hydrogen atom. It is hoped to test this experimentally. It may be of significance that anisoles and 2:5-dihydroanisoles invariably metallate in the *ortho*-position, i.e. the *ortho*-anions are the most readily formed.

The ease of reductive fission is also altered if the energy of formation of the transition state is altered in other ways. If a negative charge is placed by salt formation on the oxygen atom of an allyl or benzyl alcohol, the fission is prevented. For example, it was shown (Birch, 1945) that $\text{PhCH}=\text{CHC}(\text{CH}_3)_2\text{OH}$ is converted by sodium and alcohol in liquid ammonia into two products: $\text{PhCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$ by reduction of the double bond, and $\text{PhCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$ by reductive fission. However, the sole product from the sodium salt $\text{PhCH}=\text{CHC}(\text{CH}_3)_2\text{ONa}$ is the dihydro-alcohol, the oxygen remaining in the molecule.

If the oxygen of an ether or alcohol is replaced by nitrogen then reductive fission of the amine is usually impossible; e.g. benzylamines, unlike benzyl ethers or alcohols, are usually unaffected by sodium in liquid ammonia. This is due to the higher energy of formation of the nitrogen anion compared with the oxygen anion: amines are very weak acids compared with alcohols. However, if the nitrogen is charged positively by quaternary salt formation it can be reductively eliminated, not as an anion, but as an electrically neutral amine. The energy of the transition state is thus greatly lowered. Although dimethylaniline gives mainly the 2:5-dihydro-derivative (Birch, 1946) phenyltrimethylammonium iodide gives benzene, and benzyltrimethylammonium iodide gives toluene, the nitrogen appearing as trimethylamine. The reaction is a variant of the well-known Emde reaction using sodium-amalgam (e.g. Emde and Kull, 1934), but is much more powerful. For example, the Emde method reduces phenyltrimethylammonium salts only with great difficulty (e.g. Emde, 1909). The sodium-ammonia method may prove a useful tool in alkaloid degradation (Clayson, 1949).

EXPERIMENTAL.

Reduction of 1:2-epoxypropane (I).

1:2-Epoxypropane (7 g.) was added to a solution of sodium (6 g.) in ammonia (200 cc.) and left until the ammonia had evaporated. The residue was cautiously decomposed with a little ice, extracted with ether (2×5 cc.), the solution dried with potassium carbonate, and the ether removed through a small but efficient column. The residue (3.2 g.) distilled completely at 80–82°, and gave the 3:5-dinitrobenzoate of isopropanol as cream needles m.p. 108–109°, undepressed by an authentic specimen.

Reduction of Some Methoxyphenylcarbinols.

With the exception of 4-methoxyphenylcarbinol, which was purchased, the carbinols were made by the Grignard reaction between methylmagnesium iodide and the appropriate aldehyde or ketone. The trouble reported in the literature in the preparation of 4-methoxyphenyldimethylcarbinol, due to dehydration, was not encountered if the Grignard product was worked up without the use of acid, and the ether solution well washed with water and dried over potassium carbonate.

Reduction was accomplished by dissolving the carbinol (10 g.) and ethanol (20 cc.) in ammonia (150 cc.) and adding sodium (2.2 mol.) in small pieces with mechanical stirring. In later experiments with the object of preparing the 4-methoxy-2:5-dihydrophenylmethyl- and dimethylcarbinol, the amount of sodium was raised to 5 mol. to ensure complete reduction of the ring. The reduction products were worked up by the addition of water (100 cc.), extraction with ether (3×25 cc.) and distillation. The products of reductive fission were redistilled over sodium to remove any traces of carbinol.

(a) 2-Methoxyphenylmethylcarbinol, b.p. 130°/16 mm. (Klages, 1903) gave 2-ethylanisole, b.p. 80°/14 mm. (7 g.) (found: C, 79.5; H, 9.0%. Calculated for $\text{C}_9\text{H}_{10}\text{O}$: C, 79.4; H, 8.8%).

The product, as might be expected (Birch, 1944), contained traces of ethyldihydroanisole, because the action of 2:4-dinitrophenylhydrazine in 2 N hydrochloric acid and steam-distillation,

left a residue which was separated by crystallisation from alcohol into two substances. The more insoluble crystallised from ethyl acetate in dark red plates, m.p. 225°, and is probably *2-ethylcyclohex-2-enone 2:4-dinitrophenylhydrazone* (found: C, 55.0; H, 5.1%. $C_{14}H_{16}O_4N_4$ requires C, 55.2; H, 5.2%); the more soluble formed orange-red needles from ethanol, m.p. 118–119°, and is probably *2-ethylcyclohex-5-enone 2:4-dinitrophenylhydrazone* (found: C, 55.2; H, 5.0%. $C_{14}H_{16}O_4N_4$ requires C, 55.2; H, 5.2%) (cf. the reduction of 2-methylanisole, Birch, 1944).

(b) 2-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) gave 2-isopropylanisole (7.4 g.) b.p. 93–95°/18 mm. (found: C, 79.8; H, 9.5%. Calculated for $C_{10}H_{14}O$: C, 80.0; H, 9.3%). 3-Methoxyphenyldimethylcarbinol (Béhal and Tiffeneau, 1908) reduced to 3-isopropylanisole, b.p. 93–95°/16 mm. (found: C, 81.1; H, 9.5%. Calculated for $C_{10}H_{14}O$: C, 80.0; H, 9.3%). This contained a trace of the 2:5-dihydro-derivative, since the action of 2:4-dinitrophenylhydrazine as above gave 3-isopropylcyclohex-2-enone 2:4-dinitrophenylhydrazone, bright red prisms from ethyl acetate, m.p. 155° (found: C, 54.6; H, 5.6%. $C_{15}H_{18}O_4N_4$ requires C, 56.6; H, 5.7%). With none of these compounds was there more than a trace of higher-boiling material from the reduction.

(c) Anisyl alcohol (with 3.0 mol. of sodium) gave a mixture of a product (A) (3.1 g.) b.p. 80°/20 mm., and (B) (4.2 g.) b.p. 135°/12 mm. Fraction (A) consisted principally of 4-methyl-2:5-dihydroanisole, because the action of dilute acid (Birch, 1944) gave 4-methylcyclohex-3-enone, semicarbazone m.p. 188°, 2:4-dinitrophenylhydrazone m.p. 122°. Fraction (B) consisted principally of 4-methoxy-2:5-dihydrophenylcarbinol (found: C, 68.9; H, 8.2%. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%) (cf. Birch, 1945). On warming on the steam-bath with 1 N sulphuric acid for ten minutes, it first dissolved and then an oil separated. This was taken up in ether, and distilled in a stream of nitrogen, b.p. 75–77°/12 mm. It was very unstable, and rapidly polymerised to a clear rubbery solid. It was not analysed for this reason, but gave rise to the derivatives expected for 4-methylenecyclohex-2-enone: the semicarbazone crystallised as cream needles from alcohol m.p. 192° (decomp.) (found: C, 57.9; H, 6.7%. $C_8H_{11}ON_3$ requires C, 58.2; H, 6.7%) (if slowly heated the derivative polymerised to a pale yellow resin without melting); and 2:4-dinitrophenylhydrazone as large flat red needles from ethyl acetate, m.p. 160–161° (found: C, 53.8; H, 4.2%. $C_{13}H_{15}O_4N_4$ requires C, 54.2; H, 4.2%).

(d) 4-Methoxyphenylmethylcarbinol (Klages, 1903) reduced to give mainly 4-methoxy-2:5-dihydrophenylmethylcarbinol (6.5 g.) b.p. 130°/14 mm. (found: C, 68.9; H, 9.3%. $C_9H_{14}O_2$ requires C, 70.1; H, 9.1%) hydrolysed by hot 5% sulphuric acid to 4-ethylidenecyclohex-2-enone b.p. 100–103°/14 mm. λ_{\max}^{mol} 2,850, ϵ_{\max}^{mol} 12,800 (found: C, 78.9; H, 8.9%. $C_8H_{10}O$ requires C, 78.7; H, 8.2%); 2:4-dinitrophenylhydrazone, dark red plates from ethylacetate m.p. 164° (found: C, 55.1; H, 4.8%. $C_{14}H_{14}O_4N_4$ requires C, 55.6; H, 4.6%); semicarbazone, cream-coloured needles from ethanol m.p. 192° (found: C, 60.2; H, 7.5%. $C_9H_{13}ON_3$ requires C, 60.3; H, 7.3%).

(e) 4-Methoxyphenyldimethylcarbinol, b.p. 130°/14 mm. (Skraup and Freundlich, 1922) gave 4-methoxy-2:5-dihydrophenyldimethylcarbinol (8 g.) b.p. 128–130°/12 mm. (found: C, 70.9; H, 9.0%. $C_{10}H_{16}O_2$ requires C, 71.4; H, 9.5%). Acid hydrolysis gave 4-isopropylidenecyclohex-2-enone (5.2 g.) b.p. 117–119°/12 mm. (found: C, 78.9; H, 8.7%. $C_9H_{12}O$ requires C, 79.4; H, 8.8%); 2:4-dinitrophenylhydrazone m.p. 157° (found: C, 56.7; H, 5.1%. $C_{15}H_{16}O_4N_4$ requires C, 57.0; H, 5.0%); semicarbazone, cream-coloured needles from ethanol, m.p. 206–207° (found: C, 61.9; H, 7.8%. $C_{10}H_{14}ON_3$ requires C, 62.2; H, 7.8%).

(f) Reduction of 1-keto-6-methoxy-1:2:3:4-tetrahydronaphthalene (Stork, 1947) (7 g.) was carried out by dissolving it in warm ethanol (25 cc.), and adding the solution with vigorous stirring to ammonia (250 cc.), followed by addition of sodium (7 g.) in small pieces. Working up and distillation of the product gave two fractions: (A) b.p. up to 100°/0.4 mm. (condenser in a freezing-mixture) and (B) b.p. 100–130°/0.4 mm. Fraction (A) was heated on the steam-bath with 1 N sulphuric acid for fifteen minutes, and the oil treated with aqueous-alcoholic semicarbazide acetate. The solid so obtained was the semicarbazone of 3-keto-1:2:3:5:6:7:8:9-octahydronaphthalene, m.p. 216°, undepressed by an authentic specimen. This is the product to be expected from 6-methoxy-1:2:3:4:5:8-hexahydronaphthalene. The

residual oil from the treatment was redistilled over sodium, (0.3 g.) b.p. 193–197°, and is probably a mixture of hexahydronaphthalenes (found: C, 89.2; H, 10.4%. Calculated for $C_{16}H_{14}$: C, 89.6; H, 10.4%.) Fraction (B) was redistilled, and the main fraction (3.4 g.) had b.p. 124–126°/0.4 mm. It solidified, and was crystallised from light petroleum (b.p. 40–60°) as massive prisms, m.p. 76–77° (2.9 g.). It analysed for *1-hydroxy-6-methoxy-1:2:3:4:5:8-hexahydronaphthalene* (found: C, 73.6; H, 9.0%. $C_{11}H_{14}O_2$ requires C, 73.3; H, 8.9%.) After refluxing with 1 N sulphuric acid for thirty minutes the pleasant-smelling *3-keto-1:2:3:5:6:7-hexahydronaphthalene* was distilled, b.p. 141°/12 mm. (found: C, 80.8; H, 8.3%. $C_{16}H_{14}O$ requires C, 81.0; H, 8.1%.) The light absorption λ_{\max} 2,900 Å, $\epsilon_{\max}^{\text{mol}}$ 13,400, is in agreement with its formulation as a conjugated doubly-unsaturated ketone. The *semicarbazone* crystallised in cream-coloured prisms from ethanol, m.p. 210–211° (found: C, 64.4; H, 7.2%. $C_{11}H_{14}ON_3$ requires C, 64.4; H, 7.3%.)

Reduction of Quaternary Ammonium Salts.

Phenyltrimethylammonium iodide (20 g.) and alcohol (15 g.) in ammonia (100 cc.) underwent a vigorous reaction with sodium (4 g.). Addition of water (100 cc.) and separation of the oil (centrifuge) gave benzene (3 g.) b.p. 80°, n_D^{19} 1.4900, 1:3-dinitro-derivative m.p. 88°, undepressed by an authentic specimen. Benzyltrimethylammonium iodide similarly gave toluene, b.p. 110°, converted to 2:4-dinitrotoluene m.p. 70°, undepressed by an authentic specimen. Benzylamine or benzyldibutylamine under the same conditions gave no hydrocarbon product.

Reduction of 3-hydroxy-1-phenyl-3-methylbut-1-ene.

The carbinol (8 g.) was reacted in ammonia (100 cc.) with finely powdered sodium amide (2 g.) and then sodium (2 g.) added. The blue colour disappeared and was replaced by a brownish-red one. Working up by addition of water, ether extraction and distillation gave 3-hydroxy-1-phenyl-3-methylbutane (7.3 g.), b.p. 130°/18 mm. (found: C, 80.5; H, 9.7%. Calculated for $C_{11}H_{16}O$: C, 80.4; H, 9.75%.) It gave the phenylurethane m.p. 140°, undepressed by an authentic specimen.

SUMMARY.

The following reductions have been carried out by the action of sodium in liquid ammonia: 1:2-epoxypropane to isopropyl alcohol; several 2- and 3-methoxyphenylcarbinols to the corresponding ethylanisoles, and some 4-methoxyphenylcarbinols preponderantly to 2:5-dihydro-derivatives, hydrolysed and dehydrated by the action of acid to 4-alkylidenecyclohex-2-enones. Phenyl- and benzyltrimethylammonium iodide give benzene and toluene respectively; the sodium salt of 3-hydroxy-1-phenyl-3-methylbut-1-ene gives solely 3-hydroxy-1-phenyl-3-methylbutane. These results are discussed in relation to the theory that such reductive fissions involve the formation of transition states containing two anions.

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PEBBLES FROM THE UPPER HUNTER RIVER VALLEY, N.S.W.

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INTRODUCTION.

This paper presents the results of an examination of samples of pebbles from Triassic (Lower Narrabeen) conglomerates, from Permian (Upper Coal Measures, Muree Beds, Branxton Beds, Greta Coal Measures) conglomerates, and from gravels of certain river terrace soils. The samples were collected during a soil survey from a number of localities between Denman and Murrurundi (localities are given in Table 1).

The geology of the area has been described by David (1907), Browne (1924), Raggatt (1929; 1938) and Dulhunty (1939), and the physiography by Browne (1924) and Sussmilch (1940). The present Upper Hunter River and its tributaries are flowing in a wide mature valley in which they are slightly entrenched owing to uplift. The valley has a floor of Permian sediments; it is bounded on the west by an escarpment of Triassic conglomerates overlain in places by a thin bed of Jurassic sediments, and capped by Tertiary basalt; the eastern side of the valley is largely in Carboniferous rocks (Kuttung series) and Permian sediments. In Tertiary and post-Tertiary times the Hunter and its tributaries have deposited alluvial flats and river gravels. Remnants of Tertiary basalts occur in parts of the valley.

The original Upper Hunter after flowing out of the resistant Carboniferous rocks followed the strike of the soft westerly dipping Permian sediments and of the Wingen fault. The river enlarged its valley on the western side by the removal, due to sapping, of the hard resistant Triassic conglomerates overlying the Permian rocks (Browne, 1924, 139). Raggatt (1938) indicated that the original eastern boundary of Triassic deposition was not far east of Muswellbrook. If this is so, then the resistant material derived from the Triassic conglomerate would probably remain, in part at least, in the river valley, particularly near its western side. Rock wastage at the present time adds material to the valley sediments. The old valley floor remains as at least two river terraces, the higher at about 150 feet above the present river level (see 1: 63, 360 Military Maps, sheets 368 and 377, zone 8). The river terraces often contain gravel which may (a) have been transported from different sources during river development; (b) have been derived by the weathering *in situ* of Permian conglomeratic beds; or (c) be derived wholly or in part from the Triassic conglomerates.

In order to characterise the pebbles derived from various sources, samples were collected from the localities shown in Table 1. Samples G3-G12, G14, G15, G18 were collected from locations thought to represent the 150-foot terrace level. Of the remaining samples given in Table I, G1 and G2 are representative of the Upper Coal Measure conglomerates; G16, the Muree conglomerate; G17, the Greta Coal Measure conglomerate. G13 was taken from a soil apparently developed on the Branxton Beds (details of these beds are given by Raggatt, 1929 and 1938).

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TABLE 1.
Description and Locality of Samples Examined.

| Sample No. | Locality. | Description. |
|------------|--|---|
| N1 | West of Temple Court, near Mur-rurundi, Co. Brisbane, Pa. Mur-rurundi, Por. 27. | Lower Narrabeen conglomerate, top of cliff, 120 ft. above ground-level. |
| N2 | " " " " | Lower Narrabeen conglomerate, 50 ft. above ground-level. |
| N3 | " " " " | Lower Narrabeen conglomerate, 3 ft. above ground-level. |
| N4 | South of Mt. Murella, Co. Brisbane, Pa. Tingaroo, Por. 217. | Lower Narrabeen conglomerate, base of cliffs. |
| N5 | West of Wingen, Co. Brisbane, Pa. Wingen, Por. 168. | Lower Narrabeen conglomerate, base of cliffs. |
| N6 | Bunnan Rd., W. of Scone, Co. Brisbane, Pa. Manbus, Por. 102. | Lower Narrabeen conglomerate, base of cliffs. |
| N7 | " " " " | Lower Narrabeen sandstone, base of cliffs. |
| N8 | West of Dartbrook Lone, Co. Brisbane, Pa. Halscott, Por. 138. | Lower Narrabeen conglomerate, top of cliffs. |
| N9 | " " " " | Lower Narrabeen sandstone, top of cliffs. |
| N10 | " " " " | Lower Narrabeen sandstone, 80 ft. below top of cliffs. |
| N11 | " " " " | Lower Narrabeen coarse sandstone, base of Triassic outcrop. |
| N12 | 8 miles N.E. of Sandy Hollow, Co. Brisbane, Pa. Yarraman, Por. 43. | Lower Narrabeen conglomerate, base of cliffs. |
| N13 | Denman-Merriwa Rd., Co. Brisbane, Pa. Denman, Por. 22. | Lower Narrabeen conglomerate, top of cliffs. |
| N14 | " " " " | Lower Narrabeen conglomerate, half-way up cliffs. |
| N15 | " " " " | Lower Narrabeen conglomerate, base of cliffs. |
| G1 | S. of Muswellbrook on Hunter River, Co. Durham, Pa. Vaux, Por. 86. | Gravel from Upper Coal Measure conglomerate. |
| G2 | S. of Kyuga, Co. Brisbane, Pa. Ellis, Por. 4. | Gravel from Upper Coal Measure conglomerate. |
| G3 | W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 9. | Gravel from soil developed on Upper Coal Measures; river terrace. |
| G4 | Kingdon Ponds, Co. Brisbane, Pa. Strathearn, Por. 47. | Gravel from soil developed on Upper Coal Measures; river terrace. |
| G5 | W. of junction of Dart Brook and Hunter R., Co. Brisbane, Pa. Strathearn, Por. 39. | Gravel from soil developed on Upper Coal Measures conglomerate. |
| G6 | S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 5. | Gravel from soil developed on Upper Coal Measures. ? River terrace. |
| G7 | S.W. of Muswellbrook, Co. Brisbane, Pa. Clanricard, Por. 3. | " " " " |
| G8 | Scone, Co. Brisbane, Pa. Scone, Por. 10. | Gravel from soil developed on Upper Coal Measures; river terrace. |
| G9 | 2 miles S. Scone, Co. Brisbane, Pa. Scone, Por. 9. | Gravel from soil developed on Upper Coal Measures. ? River terrace. |
| G10 | Near junction of Pages and Hunter R., Co. Durham, Pa. Russell, Por. 347. | " " " " |
| G11 | Hunter R., S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 1. | Gravel from soil developed on Upper Coal Measures; river terrace. |
| G12 | Dart Brook, Co. Durham, Pa. Strathearn, Por. 35. | Gravel from soil developed on Upper Coal Measures; probable Triassic contamination; ? river terrace or colluvial slope. |
| G13 | St. Helier's Brook, Co. Durham, Pa. Russell, Por. 8. | Gravel from soil developed on Braxton Beds. |

TABLE 1.—*Continued.*
Description and Locality of Samples Examined.—Continued.

| Sample No. | Locality. | Description. |
|------------|---|---|
| G14 | Muswellbrook, Co. Durham, Pa. Rowan, Por. 139. | Gravel from soil developed on Branxton Beds; river terrace. |
| G15 | Muswellbrook, Co. Durham, Pa. Rowan, Por. 2. | Gravel from soil developed on Branxton Beds; ? river terrace. |
| G16 | N.E. Muswellbrook, Co. Durham, Pa. Rowan, Por. 57. | Gravel from soil developed on Muree Beds. |
| G17 | 1 mile E. Muswellbrook, Co. Durham, Pa. Rowan, Por. 181. | Conglomerate from the Greta Coal Measures. |
| G18 | 7 miles S. Muswellbrook, Co. Durham, Pa. Vaux, Por. 3. | Gravel from soil developed on Upper Coal Measures; river terrace. |

The soils from which the pebbles were collected fall into two main groups which include all the gravelly soils of the area. These are:

(1) Soils related to the Red-brown Earths. This group of soils generally has a surface A_1 horizon of dark brown to dark grey-brown loam or clay-loam over a B_1 illuvial horizon of brown clay. Lime is sporadic and may or may not show an accumulation in the B_2 horizon. The deep subsoil (BC horizon) becomes gradually yellowish. G3-9, G11-15 and G17-18 all belong to this group, with some variation in the profile morphology, chiefly as regards colour of the B_1 horizon, which varies from red-brown in G9 and G12 to dark brown in G3, 7, 14, 17, 18, and greyish yellow in G5. Most of the terrace soils fall into this group.

(2) Soils related to the Black Earths. These generally have a well structured dark brown clay surface which becomes browner with depth; a zone of lime accumulation occurs in the BC horizon. G10 belongs to this group.

G16 was taken from the surface of a podsollic soil developed on the Muree Beds. The soil description has no significance because it is not a type represented on the river terraces.

EXAMINATION OF SAMPLES.

(a) Fundamental Properties. Sedimentary materials have a number of fundamental properties which can be used to provide data for descriptive purposes. Composition, size, shape and roundness of the pebble samples were examined by means of lithology counts, mechanical analysis (giving the variation in size of the pebbles and the amount of sorting), description of the roundness and sphericity.

Lithological Composition. Lithology counts of the kinds of rock in the pebbles contained in a conglomerate, river gravel or other material give precision to descriptions of these sediments, and if a sufficiently large number of samples is collected the results can be treated statistically. Conglomerates naturally vary somewhat in lithology from place to place even if belonging to the same bed. The diagnostic value of lithology counts is indicated in recently published papers by Allen (1949) and Plumley (1948). Materials which have been transported considerable distances will have lost their softer and more easily weatherable pebbles and will consist mainly of the most resistant types of rock such as quartz and chalcedony.

Mechanical Composition. One of the fundamental properties of sedimentary fragments is size, and the size distribution of the constituents is often

characteristic, e.g. in dune sands. The size is important in connexion with the action of the transporting agent. When all the fragments in a sediment are found within one or two grade-sizes the sediment is considered to be well sorted.

In describing conglomerates the proportion of pebbles to matrix is of interest as it is considered unlikely that a very fine-grained clayey matrix such as that present in the Lower Narrabeen conglomerate could be deposited at the same time as large pebbles, a decrease in stream or current velocity being indicated (Plumley, 1948, 544).

Roundness and Sphericity of Pebbles. Roundness is a measure of the curvature of the corners and edges of fragments, and is expressed as a ratio to the average curvature of the fragment as a whole, independent of its form. This is based on the curvature of surfaces as discussed by Thomson and Tait (1879, 101). Roundness indicates wear, probably by transport, but is difficult to interpret as different sized pieces of the same material in the same bed may, and generally do, show different degrees of roundness. Allen (1949, 310) states that the estimation of "roundness" is not yet satisfactorily measured for statistical treatment.

The shape is important in the selective transportation of fragments. Shape may be a useful feature when comparing pebbles believed to be from the same source and to have undergone similar conditions of transport. The final shape which rock materials will assume on continued wear has not yet been determined with any degree of certainty (Rayleigh, 1942; 1944). It is probably only homogeneous material, fine and even grained, non-laminated, or from thick even beds among sedimentary rocks which will tend to assume a spherical shape. Observation of pebbles in a number of situations indicates that lamination, bedding and jointing are important original factors.

(b) Method of Examination.

Preliminary Treatment.

(i) *Conglomerates.* The field samples were carefully crushed in an iron mortar to free the pebbles from the matrix without breaking them. Some samples had a matrix harder than the pebbles and no unbroken pebbles could be obtained. The crushed material was quartered down until a representative sample of 2,000 to 3,000 gm. was obtained. All examinations were made on these samples.

(ii) *Gravelly Soils.* The pebbles were separated by washing out the soil and representative samples obtained as in (i).

Mechanical Analysis. The size composition of the pebbles in all samples was obtained by sieving through a set of sieves with square mesh openings of 1, $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$ inch diameter (approximately 25, 12.5, 6.25 and 3 mm. respectively). These sizes fall within the Wentworth (1922) pebble grade, 64—4 mm., with the exception of the smallest. It was not possible to obtain sieves giving the Wentworth scale which would have been desirable for comparison with pebbles described from other localities. The results of the mechanical analyses are given in Tables 3, 6 and 9. (All tables appear at the end of this paper.)

Lithology Counts. The rock types were identified in the $-1 + \frac{1}{2}$ in. grade of the pebble samples from soils and Permian conglomerates, and in the $-\frac{1}{2} + \frac{1}{2}$ in. grade of the Lower Narrabeen conglomerates. The total number of pebbles present in each of these grades was identified, and amounted to between 100 and 150 in the soil pebble samples, and 50 to 100 in the conglomerates (see Tables 2, 5 and 8).

Determination of Roundness of Pebbles. The roundness of jasper, chalcedony and chert pebbles was determined in samples of the soils and Permian conglomerates, $-1 + \frac{1}{2}$ in. grade with the exception of three samples, Nos. G1,

TABLE 2.
Lithology of Pebbles in the $-\frac{1}{2}+\frac{1}{4}$ inch Grade, Lower Narrabeen Conglomerate.
(Percentage by Number.)

| Sample No. | N6 | N8 | N9 | N10 | N11 | N12 | N14 | N15 |
|--------------------------------|----|----|----|-----|-----|-----|-----|-----|
| Rock types : | | | | | | | | |
| Quartz | 3 | 6 | 15 | — | 3 | — | — | — |
| Jasper | 10 | 6 | 8 | 23 | 10 | 15 | 4 | — |
| Chert and chalcedony | 46 | 63 | 38 | 38 | 41 | 49 | 46 | 65 |
| Sedimentary* | 36 | 22 | 38 | 38 | 45 | 20 | 22 | 34 |
| Quartzite | — | — | — | — | — | — | 1 | — |
| Acid igneous† | — | 1 | — | — | — | 15 | 21 | — |
| Tuff | 3 | — | — | — | — | — | 2 | — |

* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

TABLE 3.
Size Composition of Pebbles in the Lower Narrabeen Conglomerate.
(Grade units are in inches ; Percentage by weight.)

| Grade. | $-1+\frac{1}{2}$. | $-\frac{1}{2}+\frac{1}{4}$. | $-\frac{1}{4}+\frac{1}{8}$. | $-\frac{1}{8}$ Coarse Sand + Matrix. |
|---------------|--------------------|------------------------------|------------------------------|--|
| Sample No.— | % | % | % | % |
| N6 | 2.0 | 4.7 | 4.0 | 89.3 |
| N7 | — | — | 2.5 | 97.5 |
| N8 | 15.6 | 22.0 | 27.0 | 36.4 |
| N9 | 3.4 | 3.0 | 0.5 | 93.1 |
| N10 | — | 8.0 | 9.3 | 82.7 |
| N12 | 21.0 | 33.0 | 18.0 | 28.0 |
| N14 | 17.0 | 43.0 | 18.0 | 22.0 |
| N15 | 15.0 | 31.0 | 23.0 | 31.0 |

TABLE 4.
Roundness and Sphericity of Pebbles from the Lower Narrabeen Conglomerate
($-\frac{1}{2}+\frac{1}{4}$ inch Grade).

| | Mean Roundness. | Mean Sphericity. | Zingg Classification.* |
|----------------|--------------------|---------------------|---------------------------|
| Sample No.— | | | |
| N6 | 0.42 | 0.75 | 11 |
| N8 | 0.54 | 0.78 | 1 |
| N9 | 0.27 | 0.75 | 11 |
| N10 | 0.40 | 0.76 | 11 |
| N11 | 0.46 | 0.71 | 1 |
| N12 | 0.50 | 0.74 | 11 |
| N14† | 0.52 | 0.75 | 11 |
| N15 | 0.56 | 0.73 | 11 |

* The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.

† Chalcedony pebbles only.

G2 and G10, in which the acid igneous rock pebbles were used because of the low content of jasper and chalcedony. In the Lower Narrabeen conglomerates all the pebbles in the $-\frac{1}{2} + \frac{1}{2}$ in. grade were used. The roundness was determined visually by comparison with Krumbein's (1941) pebble images (see Tables 4, 7 and 10).

Shape of Pebbles. The shape was determined by Krumbein's intercept method (1941) which is based on a triaxial ellipsoid as the reference solid to which a pebble is compared (this implies that a sphere is the final shape towards which a pebble is progressing through abrasion, a fact which is not yet proved). It is therefore necessary to define the three diameters of a pebble as mutually perpendicular intercepts. The three diameters measured are designated as *a* (long), *b* (intermediate) and *c* (short). After the measurements have been made the ratios *b/a* and *c/b* are obtained and these are laid off on the axes of Krumbein's chart from which the sphericity figure is obtained. The Zingg (1935) pebble shape, based on the ratio of *b/a* to *c/b* is also given in Tables 4, 7 and 10. The measurements were made with a gauge similar to that illustrated by Krumbein (1941). An average of thirty randomly chosen pebbles of jasper and chalcedony from the $-1 + \frac{1}{2}$ inch grade of soils and Permian conglomerates was measured to give the figures in Tables 7 and 10. Similar representative pebbles from the Lower Narrabeen conglomerates were used for the figures in Table 4.

DISCUSSION OF RESULTS.

Lower Narrabeen Conglomerate.

The Triassic rocks of the district were first described by Carne (1906, 55), who noted the "chalcedonic and jasperoid constituents of the pebbles and boulders. Red and green are the predominant colours, whilst ordinary white quartz pebbles are rarer and smaller". He considered that the pebbles were derived from altered Carboniferous and Devonian sediments to the north. On the other hand the Permian conglomerates are of quartz pebble character which distinguishes them from the Triassic conglomerates (*ibid.*, 53). Raggatt (1938), however, found difficulty in distinguishing the Permian from the Triassic conglomerates on lithological grounds alone. Dulhunty (1939) noted the presence of an upper portion about 250 ft. thick of homogenous medium-grained sandstone and a lower, 400 ft. thick, of conglomerate "being made up of coarse-grained sandstone packed with small rounded pebbles, mainly white quartz with a limited amount of red and black jasper" (*ibid.*, 32).

The Lower Narrabeen conglomerate was sampled at the base, middle and top of the lower portion of these Triassic beds. When examined in hand specimen, the basal Narrabeen conglomerate between Murrurundi and Denman is seen to be massive with a fine-grained, firmly cemented, clayey matrix which encloses pebbles of chalcedony, jasper, clayey sandstone and quartz, varying in size from about one-eighth inch to over one inch in diameter, the majority being about one-half inch in diameter. The matrix is very seldom sandy, and may be so hard that it is impossible to remove pebbles without breaking them. From this it may vary to softer material and finally to sandy lenses with few pebbles. On superficial examination the bed appears to be fairly uniform both laterally and vertically, but the mechanical analyses indicate that this is not so. On weathering the softer pebbles and matrix are removed first, leaving jasper and chalcedony prominent. The lithological composition is given in Table 2, which shows that chert and chalcedony are the most abundant constituents, followed by various sedimentary rocks. Quartz is not abundant except in N9; only two samples, N12 and N14, contain appreciable amounts of acid igneous rock pebbles. Jasper is always more plentiful than black chert; greenish cherty pebbles which are so noticeable on weathered surfaces are not plentiful.

The variation in lithology of the pebbles in the Lower Narrabeen conglomerate can be shown thus :

| <i>Types of Pebbles.</i> (Percentage by Number.) | | | | | |
|---|-----------------|---------|-------------|--------------|---------------|
| | Quartz. | Jasper. | Chalcedony. | Sedimentary. | Acid Igneous. |
| Upper | 10 | 7 (57) | 50 | 30 | $\frac{3}{2}$ |
| Middle | — | 13 (55) | 42 | 30 | 10 |
| Lower | 1 $\frac{1}{2}$ | 9 (59) | 50 | 34 | 5 |

These figures are the averages of only a limited number of samples, but the ratio of jasper plus chalcedony to sedimentary rocks appears to be rather constant, and can be taken as characteristic of these beds.

Table 3 gives the distribution of sizes of the pebbles for the same samples and the variation in proportion of pebbles to matrix. It is unsafe to generalise from few samples, but the basal part of these beds appears to have a larger pebble content than the upper.

The mean roundness and mean sphericity are given in Table 4. Although the first impression given by the pebbles is that of roundness, close examination of the edges indicates that the rounding is only moderate when compared with Krumbein's roundness images (1941, Pl. 1). Individual pebbles may reach a roundness of 0·8 or 0·9, but the mean is between 0·42 and 0·56, with one sample, N9, having a roundness of only 0·27, which indicates sharp broken edges (care was taken during the initial crushing not to break pebbles so that this figure is a natural one).

The shape of the pebbles, given as mean sphericity, is much more uniform than the roundness ; it varies between 0·71 and 0·78, the pebbles falling into Zingg's (1935) spherical class, with the exception of N8 and N11, which are disc-like. The pebbles measured were largely chalcedony, which, being homogeneous, would tend to assume a spherical form rather than any other.

Permian Conglomerates.

The Permian conglomerates are represented by samples G1 and G2 from the Upper Coal Measures, G13 from the Branxton Beds, G16 from the Muree Beds, and G17 from the Greta Coal Measures (see Table 1). The distribution and lithology of these formations in the Upper Hunter River Valley has been described by Raggatt (1929 ; 1938). The Muree Beds have the greatest surface area.

The lithology of these samples is given in Table 5. The Upper Coal Measure beds are characterised by the absence of quartz and jasper, the limited quantity

TABLE 5.
Lithology of Pebbles in the —1+ $\frac{1}{2}$ in. Grade from Permian Conglomerates.
(Percentage by number.)

| Sample No. | G1. | G2. | G13. | G16. | G17 |
|-------------------------|-----|-----|------|------|-----|
| Rock types— | | | | | |
| Quartz | — | — | — | 9 | — |
| Jasper | — | — | 21 | 27 | — |
| Chalcedony and chert .. | 3 | 7 | 10 | 5 | 39 |
| Sedimentary* | 16 | 3 | 40 | 59 | 18 |
| Quartzite | — | 7 | — | — | 2 |
| Acid igneous† | 81 | 69 | 28 | — | 24 |
| Basalt | — | 14 | 1 | — | — |

* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

of chalcedony, the rather small quantity of sedimentary rock pebbles, and the preponderance of acid igneous rock pebbles. The basalt pebbles in G2 may be due to contamination. The sample from the Brantxton Bed is characterised by jasper and chalcedony, but the most prominent constituent is sedimentary

TABLE 6.
Size Composition of Pebbles in the Permian Conglomerates.
(Grade units in inches ; percentage by weight.)

| Grade | -2+1. | -1+ $\frac{1}{2}$. | - $\frac{1}{2}$ + $\frac{1}{4}$. | - $\frac{1}{4}$ + $\frac{1}{8}$. | - $\frac{1}{8}$ (Coarse Sand and Matrix). |
|-------------|-------|---------------------|-----------------------------------|-----------------------------------|--|
| Sample No.— | % | % | % | % | % |
| G1 | 20.0 | 13.0 | 41.0 | 18.0 | 8.0 |
| G2 | 66.4 | 25.1 | 4.0 | 1.1 | 3.3 |
| G13 | 52.5 | 35.7 | 11.8 | — | — |
| G16 | 9.6 | 19.0 | 47.8 | 4.2 | 19.1 |
| G17 | 24.5 | 28.6 | 37.6 | 7.0 | 2.2 |

TABLE 7.
Roundness and Sphericity of Pebbles from the Permian Conglomerate
(-1+ $\frac{1}{2}$ inch Grade).

| | Mean Roundness. | Mean Sphericity. | Zingg Classification.* |
|-------------|--------------------|---------------------|---------------------------|
| Sample No.— | | | |
| G1† | 0.50 | 0.78 | 11 |
| G2† | 0.55 | 0.77 | 11 |
| G13 | 0.49 | 0.86 | 11 |
| G16 | 0.44 | 0.76 | 11 |
| G17 | 0.55 | 0.77 | 11 |

* The shape of pebbles in Zingg's classification is : Class I, discs ; Class II, spherical ; Class III, blades ; Class IV, rod-like.

† Acid igneous rock pebbles ; the remainder are jasper and chalcedony pebbles.

TABLE 8.
Lithology of Pebbles in the -1+ $\frac{1}{2}$ in. Grade of River Terrace Soils.
(Percentage by Number.)

| Sample No. | G3. | G4. | G5. | G6. | G7. | G8. | G9. | G10. | G11. | G12. | G14. | G15. | G18. |
|----------------------|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|
| Rock types— | | | | | | | | | | | | | |
| Quartz | 3 | 5 | 3 | — | 4 | 4 | 5 | 2 | 16 | 6 | — | 2 | 6. |
| Jasper | 4 | 10 | 15 | — | 8 | 14 | 15 | — | 26 | 4 | 2 | 31 | 29 |
| Chalcedony and chert | 37 | 75 | 64 | 69 | 40 | 79 | 54 | 6 | 35 | 67 | 42 | 31 | 9 |
| Sedimentary* | 13 | 3 | 3 | 15 | 9 | 2 | 12 | 13 | 11 | 14 | 22 | 21 | 1 |
| Quartzite | — | — | — | — | — | — | — | — | — | — | — | — | 1 |
| Acid igneous† | 29 | 6 | 10 | 16 | 33 | — | 12 | 34 | 12 | 8 | 29 | 14 | 27 |
| Basalt | 12 | 1 | 3 | — | 5 | 1 | 3 | 37 | 2 | — | 4 | — | 26 |

* Sedimentary rocks include claystone, sandstone (fine and coarser), indurated shale.

† Acid igneous rocks include rhyolite, felsite and allied types.

rock; acid igneous rock pebbles are also prominent. The Muree Bed contains quartz, jasper, chalcedony and sedimentary pebbles but no acid igneous rocks, whereas the Greta Coal Measure conglomerate has conspicuous igneous rock pebbles with no quartz and jasper, although chert and chalcedony pebbles are plentiful.

The variation in size of the pebbles is given in Table 6. G2 (Upper Coal Measures) and G13 (Branxton Beds) are fairly well graded, but the pebbles of other samples are not. In G2 and G13 the maximum grade is in the $-2+1$ inch grade. A slight maximum occurs in the other samples in the $-\frac{1}{2}+\frac{1}{4}$ inch grade. The percentage of coarse sand and matrix is conspicuous only in G16 (Muree).

The mean roundness and sphericity are given in Table 7. The mean roundness varies from 0.44 (Muree) to 0.55 (Upper Coal Measures and Greta). The sphericity varies from 0.77 (Upper Coal Measures and Greta) to 0.86 (Branxton). The pebbles from all these samples fall into Zingg's (1935) spherical class.

River Terrace Soils.

The soils from which pebbles were obtained are described in the Introduction. All the samples with the exception of G10 were from Red-brown Earth on the river terraces.

The lithology is given in Table 8, which is a simplification of the rock types actually recorded, which are: quartz (milky), chalcedony and chert (red, white, grey, banded), jasper, quartzite, shale (white, grey, indurated), sandstone (coarse, fine, brown, yellow, ferruginous, clayey, chalky), claystone, ferruginous mudstone, tuff, acid igneous (mainly lavas; coarse, fine, altered, white, pale green, banded), rhyolite, porphyry, basalt, weathered basalt. There is thus a much greater variety in the gravels than in the Lower Narrabeen conglomerate.

Quartz is present in all but two of the samples in small amounts only, and is conspicuous (16%) in G11 collected from above the Upper Coal Measures.

Jasper and chalcedony are prominent constituents in all the samples except G10. The range is from 38% to 93% (G8 from near Scone). G3, G7, G14, G18 are low in jasper and chalcedony and high in acid igneous rocks (when compared with other samples from the area):

| | G3. | G7. | G14. | G18. |
|-----------------------|-----|-----|------|------|
| | % | % | % | % |
| Jasper and chalcedony | 41 | 48 | 44 | 38 |
| Acid igneous .. | 29 | 33 | 29 | 27 |

These samples were all collected from above the Upper Coal Measures and Branxton Beds whose jasper and chalcedony contents are rather low and acid igneous rock contents rather high. It may be presumed therefore that the parent material of the soil is in part at least the underlying rock.

Of those samples with a high percentage of jasper and chalcedony a number contain varying percentages of acid igneous rock pebbles up to 12% in G9 and G11. The large amount of jasper and chalcedony appears to have been added to the original weathering product of the Upper Coal Measures and other beds, although contamination with material from the Muree Beds might have the same effect.

Sedimentary rock pebbles occur in practically all of these samples and their source could be any of the Permian beds in the valley. Table 5 shows that the Muree beds contained nearly 60% of this type of pebble. The largest percentages of sedimentary rock pebbles occur in those samples rather low in jasper and chalcedony and therefore strengthens the case for rather less contamination of these samples.

Basalt pebbles occur in small amounts in a number of these samples, G18 containing 26% and G3, 12%. G6, G12 and G15 contain no basalt, and the remaining samples only small amounts. In view of the fact that one of the

TABLE 9.
Size Composition of Pebbles in the River Terrace Soils.
(Grade units in inches; percentage by weight.)

| Grade | $-2+1.$ | $-1+\frac{1}{2}.$ | $-\frac{1}{2}+\frac{1}{4}.$ | $-\frac{1}{4}+\frac{1}{8}.$ | $-\frac{1}{8}$ (Coarse Sand and Fine Sand). |
|---------------|---------|-------------------|-----------------------------|-----------------------------|--|
| Sample No.— | % | % | % | % | % |
| G3 | 42.2 | 21.0 | 25.0 | 6.4 | 5.4 |
| G4 | 44.8 | 25.0 | 21.7 | 4.0 | 4.3 |
| G5 | 4.1 | 16.8 | 26.0 | 15.9 | 35.2 |
| G6 | 33.0 | 37.4 | 18.5 | 4.8 | 6.3 |
| G7 | 57.8 | 21.5 | 11.6 | 2.7 | 4.7 |
| G8 | 26.5 | 23.4 | 44.8 | 7.0* | 7.6 |
| G9 | 55.5 | 30.3 | 11.1 | 1.0 | 1.9 |
| G10 | 62.5 | 26.1 | 6.2 | 1.4 | 4.0 |
| G11 | 27.5 | 32.0 | 32.1 | 7.7 | — |
| G12 | 57.5 | 23.1 | 14.3 | 2.5 | 2.4 |
| G14 | 91.3 | 8.7 | — | — | — |
| G15 | 47.7 | 19.1 | 17.6 | 5.6 | 10.9 |
| G18 | 76.0 | 24.0 | — | — | — |

Upper Coal Measure conglomerates contained basalt pebbles it seems probable that little significance can be attached to small quantities of basalt in these samples, whereas large quantities indicate either proximity to basaltic flow remnants, plugs or sills, or to addition by stream transport of pebbles from an

TABLE 10.
*Roundness and Sphericity of Pebbles from the River Terrace Soils ($-1+\frac{1}{2}$ in.
Grade; Jasper and Chalcedony).*

| Sample No.— | Mean Roundness. | Mean Sphericity. | Zingg Classification.* |
|--------------|--------------------|---------------------|---------------------------|
| G3 | 0.48 | 0.72 | 11 |
| G4 | 0.48 | 0.73 | 11 |
| G5 | 0.46 | 0.76 | 11 |
| G6 | 0.47 | 0.73 | 11 |
| G7 | 0.51 | 0.76 | 11 |
| G8 | 0.53 | 0.77 | 11 |
| G9 | 0.52 | 0.76 | 11 |
| G10† | 0.33 | 0.73 | 11 |
| G11 | 0.50 | 0.78 | 11 |
| G12 | 0.51 | 0.73 | 11 |
| G14 | 0.49 | 0.77 | 11 |
| G15 | 0.52 | 0.78 | 11 |
| G18 | 0.55 | 0.75 | 11 |

* The shape of pebbles in Zingg's classification is: Class I, discs; Class II, spherical; Class III, blades; Class IV, rod-like.

† Acid igneous rock pebbles.

outcrop of basalt. Many of the basalt pebbles in these soils are weathered, and it is possible that many originally present may have disappeared during soil formation.

The only soil belonging to the Black Earth group (G10) contains very little quartz and chalcedony, but 37% of basaltic pebbles and 34% of acid igneous rock pebbles. As this sample was collected from near the junction of the Pages and Upper Hunter Rivers, it is possible that the basaltic pebbles have been transported there. The influence of the basalt is clearly to be traced in the formation of a Black Earth. If the basalt were *in situ*, it is probable that acid igneous rock pebbles would not be present.

The variation of sizes of the pebbles is given in Table 9. In general the pebbles are not well sorted except in G14 and G18, with a maximum of 91% and 76% in the $-2+1$ inch grade. These are most probably river gravels, as the grading of the Permian sediments is not particularly good. G7, G9, G10, G12 also show a fairly strong maximum in the same grade. The Permian conglomerates also show a maximum in this grade, where sorting is at all good, but the Lower Narrabeen conglomerates examined here are much finer grained with a maximum in the $-1+\frac{1}{2}$ or $-\frac{1}{2}+\frac{1}{4}$ inch grade. Without additional samples it would be unwise to generalise further from these figures.

Figures for the roundness and sphericity are given in Table 10. The roundness for pebbles from the Red-brown earth soils varies from 0.46 to 0.55, which indicates that the edges are not at all well-rounded and that many broken pebbles are present. The mean roundness for sample G10 is only 0.33. The mean sphericity is fairly constantly high, ranging from 0.72 to 0.78. It appears to have little diagnostic value, except to indicate similarity, in this series of samples. All the pebbles fall into Zingg's spherical class. It would appear that the same kind of environment existed for all these pebbles, though the homogenous material (jasper and chalcedony) would tend to assume this shape on abrasion irrespective of environment.

CONCLUSIONS.

The number of samples examined was insufficient to treat the results statistically, but the following conclusions appear to be justified.

Detailed lithological examination of the various conglomerates has given precision to the description of these beds, and this information can be used to suggest the origin of the various gravelly soils which have developed on the river terraces in the area examined. Further evidence is expected from an examination of the heavy mineral residues of these soils. Contamination with material either from the Lower Narrabeen conglomerate or the resorting and redistribution of the materials of the Permian beds is indicated. Acid igneous rock pebbles appear to be derived from various members of the Permian in a number of instances. The presence of basalt pebbles indicates either nearness to source or transport from a source at no great distance. The degree of sorting of several of the terrace gravels indicates the action of rivers, but it seems that transport was not for long distances, as no pebbles from the Kuttung glacial beds were found. Little can be inferred from the figures for roundness and sphericity; the pebbles are not as well water-worn as previous descriptions indicate, which shows that transport has not been from long distances or continuous. It is probable that no further alteration of shape or roundness has been made by the action of the Upper Hunter and its tributaries. All the pebbles are of the same type except some of those in the Lower Narrabeen conglomerates which are, in addition, simpler lithologically. It is suggested that the weathering *in situ* of the Permian beds is an important factor in the soils developed on the terraces in some localities.

ACKNOWLEDGEMENTS.

We wish to acknowledge with thanks the courtesy of Professor C. E. Marshall, Department of Geology, University of Sydney, in allowing us the use of a laboratory and certain equipment, and of Dr. E. G. Hallsworth, School of Agriculture, University of Sydney, in lending us other basic equipment.

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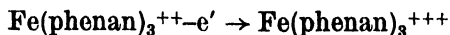
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THE RESOLUTION OF THE TRIS o,PHENANTHROLINE FERROUS ION AND THE OXIDATION OF THE ENANTIOMORPHOUS FORMS.

By F. P. DWYER, D.Sc.
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Manuscript received, November 10, 1949. Read, December 7, 1949.

When o,phenanthroline is added to ferrous salt solutions, red compounds result which have been shown to have the constitution $\text{Fe(phenan)}_3\text{X}_2\cdot n\text{H}_2\text{O}$ (Blau, 1898). The tris o,phenanthroline ferrous ion is reversibly oxidisable to the blue tris o,phenanthroline ferric ion the redox potential for the reaction



being 1.12 volts (Smith and Richter, 1944 ; Dwyer and McKenzie, 1947). In this paper the resolution of the ferrous complex and the oxidation of the enantiomorphous forms is described.

The resolution was carried out through the antimonyl tartrates, and it was found that on adding potassium antimonyl tartrate to a racemic solution of Fe(phenan)_3^{++} in water the l-complex d-antimonyl tartrate separated as a highly insoluble precipitate, whilst the d-complex remained in solution and could be precipitated from the mother liquid as the sparingly soluble perchlorate. The perchlorate of the laevo form was obtained by dissolving the antimonyl tartrate precipitate in caustic soda solution (thus destroying the antimonyl tartrate radicle) and adding sodium perchlorate. The active perchlorates were more soluble in water than the racemate.

The resolution of the analogous tris o,phenanthroline ruthenium II and nickel II complexes and recently that of the osmium II complex has been carried out in a similar way (Dwyer and Gyarfas, 1949*a, b, c*). In all of these complexes the d-Me(phenan)₃ d-antimonyl tartrate (Me = Ru II, Ni II, Os II), formed the highly insoluble compound. It is reasonable to suppose, therefore, that the form of the ferrous complex precipitated as the d-antimonyl tartrate has the same configuration as the dextrorotatory Ru II, Ni II and Os II complexes. The sign of the rotation is of no significance since all these ions possess a strongly abnormal rotatory dispersion, the investigation of which is now being carried out, and will be published in a subsequent communication.

The optical forms were more stable than the active forms of the tris 2 : 2' dipyridyl ferrous ion resolved by Werner (1912*a*). Thus whilst the rotations of solutions of this substance dropped to half of its original value in half an hour the phenanthroline complexes in solution have a half life of approximately one hour, and the solids possess some rotation even after a period of six months. The same relation was found between the stabilities of the corresponding Ni(dipy)_3^{++} and Ni(phenan)_3^{++} complexes (Morgan and Burstall, 1931 ; Dwyer and Gyarfas, 1949*b*). On standing from a racemic solution of the ferrous complex containing excess antimonyl tartrate, the whole of the complex precipitated slowly as the l-complex d-antimonyl tartrate, leaving a colourless solution behind. This is due to the racemisation of the solution. The equilibrium between the d and l complex ions is being shifted towards the latter, which is continuously eliminated from the solution as the insoluble antimonyl

tartrate, and finally none of the d-complex remains. A similar reaction was, observed on the resolution of the trioxalato chromiates with strychnine (Werner 1912b).

In a previous paper (Dwyer and Gyarfás, 1949a), the oxidation of the enantiomorphous forms of the tris o,phenanthroline ruthenium II complex was described. It was found that on oxidation of the active solutions of this complex the solutions of the blue ruthenium III complex were still optically active, although the magnitude of rotation was different, and that on reduction the ruthenium II complex was obtained with its rotation unchanged. If the same experiment is carried out on the active tris o,phenanthroline ferrous ion at room temperature, as stated by the authors in a note in *Nature* (Dwyer and Gyarfás, 1949), the rotation is lost on oxidation due to the rapid racemisation of the ferric complex. However, at 6° C. the rate of racemisation being reduced, active solutions of the ferric complex could be obtained. The rate of racemisation even at 6° C. was too rapid to permit measurement of the specific rotation with any degree of accuracy, but it is approximately 60% of that of the ferrous complex in the Nad line.

EXPERIMENTAL.

Owing to the racemisation of the active substances standard solutions could not be made up for measurements of rotations. The determinations of specific rotations was done by shaking the active substance in ice-cold water for a few seconds, filtering off the undissolved material on the filter pump, and measuring the angle of rotation immediately. The concentration of the solution was determined subsequently by comparing it with a standard solution in a photo-electric colorimeter.

A 2 dm. tube was used in all experiments.

l-Tris o,Phenanthroline Iron II d-Antimonyl Tartrate Tetrahydrate.

d,l Tris o,phenanthroline ferrous sulphate was prepared by the addition of finely divided o,phenanthroline monohydrate (2.2 g.) to a solution of ferrous sulphate heptahydrate (1.2 g.) in water (100 ml.). The mixture was stirred until the phenanthroline had dissolved completely. To the deep red solution of tris o,phenanthroline ferrous sulphate a solution of potassium d-antimonyl tartrate (2.5 g.) in water (20 ml.) was added slowly. On scratching the sides of the vessel a dark red crystalline substance was obtained. The reaction mixture was cooled rapidly in ice and the precipitate filtered off immediately. The crystalline substance was found to be pure l-tris o,phenanthroline ferrous d-antimonyl tartrate. It was practically insoluble in water but could be recrystallised by solution in 0.1 N caustic soda (50 ml.) and reprecipitation with the addition of acetic acid and a little potassium antimonyl tartrate. The substance crystallised in dark red needles.

A 0.0100% solution in water gave $\alpha_D = -0.19^\circ$, whence $[\alpha]_D^{25} = -950^\circ$.

Found: Fe=4.37%; Sb=19.54%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{SbO}_2\text{C}_4\text{H}_4\text{O}_6)_2 \cdot 4\text{H}_2\text{O}$: Fe=4.50%; Sb=19.63%.

l-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The l-tris o,phenanthroline ferrous d-antimonyl tartrate was dissolved in approximately N/20 caustic soda (50 ml.) by shaking at about 5° C., and the solution filtered. Sodium perchlorate solution was then added slowly and on scratching the sides of the vessel a red crystalline precipitate was obtained. This, after immediate filtration, washing with ice water and drying, gave the pure l-perchlorate in micropismatic needles. The substance was appreciably soluble in water, very soluble in acetone and sparingly soluble in alcohol.

A 0.0144% solution in water gave $\alpha_D = -0.41^\circ$, and a 0.0126% solution in water gave $\alpha_D = -0.35^\circ$, whence $[\alpha]_D^{25} = -1416^\circ$.

Found: Fe=6.53%; N=10.04%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$: Fe=6.58%; N=9.90%.

d-Tris o,Phenanthroline Iron II Perchlorate Trihydrate.

The mother liquid of the original precipitate with potassium antimonyl tartrate was strongly dextrorotatory. The cold solution (5° C.) was treated immediately with sodium perchlorate solution. (Avoiding an excess to prevent the precipitation of potassium perchlorate.) The resulting red crystalline precipitate was the pure perchlorate of the dextro complex forming micropisms and needles.

A 0.0111% solution in water gave $\alpha_D = +0.32^\circ$ and a 0.0123% solution in water gave $\alpha_D = +0.35^\circ$, whence $[\alpha]_D^{25} = +1432^\circ$.

Found: Fe = 6.53%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$: Fe = 6.58%.

SUMMARY.

Tris o,phenanthroline iron II perchlorate has been resolved through the d-antimonyl tartrate. The optical forms were stable in the solid state for some months, but racemised rapidly in solution. After oxidation of the enantiomorphous forms with ceric sulphate at 6° C., the resulting blue iron III complex was found to possess a fleeting activity.

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A NOTE ON SOME 4-METHOXYBENZENE-AZO DERIVATIVES OF RESORCINOL

By P. H. GORE, M.Sc.,
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Manuscript received, October 27, 1949. Read, December 2, 1949.

On coupling molar equivalents of diazotised p-anisidine with resorcinol monacetate in alkaline solution, both a mono- (I, 33%) and a bis-azo compound (II, 29%) were obtained, but no appreciable amounts of acetyl derivatives could be isolated. The same two products were also isolated (I, 47%; II, 17%) by coupling molar proportions of diazotised p-anisidine with resorcinol in the presence of alkali. (I) must be 2:4-dihydroxy-4'-methoxyazobenzene.

The formation of bis-azo compounds by coupling diazotised aniline with resorcinol was first reported by Wallach and Fischer (1882) (cf. Typke, 1877; Will and Pukall, 1887). It was later found that the pH of the solution determines which of two bis-azo isomers is formed. In the presence of sodium carbonate or acetate, 2 moles of diazotised aniline couple with one of resorcinol to give 2:4-bis(benzeneazo)-1:3-dihydroxybenzene (Kostanecki, 1888; cf. Liebermann and Kostanecki, 1884; Kostanecki, 1887; Orndorff and Ray, 1907), whilst in dilute excess sodium hydroxide 4:6-bis(benzeneazo)-1:3-dihydroxybenzene is formed (Kostanecki, 1888).

It is thus reasonable to assume that the structure of the bis-azo compound (II) formed above is 4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene.

On coupling molar proportions of diazotised p-anisidine with resorcinol monomethyl ether, two compounds $C_{14}H_{14}O_3N_2$ are formed (cf. Hodgson *et al.*, 1934). One isomer, m.p. 116° , occurs to about 90%, the other, m.p. 134° , to about 10% in the mixture. Separation was achieved by exhaustive steam distillation, the higher melting isomer being slightly volatile. This isomer probably identical with the hydroxyazo compound, m.p. 121° (crude), isolated by Cumming and Ferrier (1925) from 4:4'-dimethoxyazobenzene by the action of light, is therefore 2-hydroxy-4:4'-dimethoxyazobenzene (III). The other isomer, m.p. 116° , would then be 4-hydroxy-2:4'-dimethoxyazobenzene (IV).

On methylation with diazomethane of (I) yields of (III) (68%) and (IV) (26%) were obtained. This result is to be expected from a hydrogen bonded o-hydroxyazo compound.

EXPERIMENTAL.

4'-methoxy-2:4-dihydroxyazobenzene (I), and 4:6-bis(4'-methoxybenzeneazo)-1:3-dihydroxybenzene (II)

(A) p-Anisidine (1 mol.) was diazotised in hydrochloric acid (3 mol.) in the usual way, and added to a freshly prepared dilute solution of resorcinol monacetate (1 mol.) in sodium hydroxide (5 mol.) at 0°C . After stirring for 30 min., the solution was made faintly acid, and the red-brown precipitate filtered off. Extraction with hot 20% acetic acid removed (I), which crystallised out on cooling, and after recrystallisation from dilute acetic acid, formed glistening carmine needles (33%), m.p. 150° , which became dull orange needles, m.p. $150\text{--}151^\circ$, on drying in the desiccator, or at 110° .

Found: N, 11.8; -OMe, 12.9%.

Calculated for $C_{13}H_{13}O_3N_3$: N, 11.5; -OMe, 12.7%.

The residue (II) crystallised from glacial acetic acid in minute brown-violet flakes, m.p. 225°, yield 29%.

Found: N, 14.8; -OMe, 16.1%.

Calculated for $C_{20}H_{18}O_4N_4$: N, 14.8; -OMe, 16.4%.

(B) Preparation as above, using resorcinol instead of its monacetate. Yields: (I), 47%; (II), 17%.

4:6-Bis(4'-methoxybenzeneazo)-1:3-dimethoxybenzene (V).

(V) was formed by methylation of (II) in boiling acetone solution with excess methyl iodide in the presence of potassium carbonate. It formed red needles from dilute acetic acid.

Found: N, 13.8%.

Calculated for $C_{22}H_{22}O_4N_4$: N, 13.8%.

2-Hydroxy-4:4'-dimethoxyazobenzene (III) and 4-hydroxy-2:4'-dimethoxyazobenzene (IV).

Preparation as for (I) and (II), using resorcinol monomethyl ether instead of resorcinol monacetate. Before acidification, the solution was extracted with ether, which removed a small quantity of red crystals of (III) (m.p., after one crystallisation from aqueous acetic acid, 127–128°). Another crop of (III) (total 5%) was obtained by acidification of the liquor, followed by exhaustive steam distillation. (III) forms glistening red monoclinic crystals from aqueous alcohol or dilute acetic acid, m.p. 134°.

Found: N, 10.8%.

Calculated for $C_{14}H_{14}O_3N_2$: N, 10.9%.

It is only slightly soluble in cold 0.5% to 10% sodium hydroxide solution.

The steam distillation residue affords (IV) (60%) after three crystallisations from aqueous acetic acid, aqueous alcohol or aqueous pyridine. From the former it crystallises in red needles, m.p. 85°, which after drying lose their solvent of crystallisation and become dull salmon coloured, m.p. 116°.

Found: N, 11.0%; -OMe, 23.9%.

Calculated for $C_{14}H_{14}O_3N_2$: N, 10.9%; -OMe, 24.3%.

The benzoyl derivative crystallises from dilute acetic acid in shimmering orange-brown flakes, m.p. 144.5°.

Found: N, 7.8%; -OMe, 16.7%.

Calculated for $C_{21}H_{18}O_4N_2$: N, 7.7%; -OMe, 17.1%.

Methylation of (I).

(I) (0.25 g.) in dry ether (50 ml.) was treated with a solution of a large excess of diazomethane (from nitrosomethylurea, 2 g.) in ether (50 ml.), and allowed to stand overnight. The filtered solution was extracted three times with 10% sodium hydroxide solution (20 ml.). The alkali extract afforded (IV) (impure, 0.07 g., 26%), the ether extract (III) (pure, 0.18 g., 68%).

ACKNOWLEDGEMENTS.

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STUDIES IN THE DEMETHYLATION OF THIOANISOLE.

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During attempts to prepare the sulphur analogues of the synthetic sex hormones stilbestrol, hexestrol and dienestrol it was not found possible to demethylate the intermediate methyl ethers and experiments were begun on the dealkylation of thioanisole (Hughes and Thompson, 1948). This paper reports further attempts using the methods successfully used with oxygen alkyl ethers.

Sodium in boiling pyridine, as used by Prey (1943) for the cleavage of phenol ethers, gave 60% thiophenol and no thioanisole was recovered.

Heating with aluminium chloride caused some demethylation, but the yields of thiophenol were low and were difficult to reproduce. With equimolecular amounts of thioanisole and aluminium chloride at 100° C. the yield of thiophenol averaged 20%, in one experiment 35% was obtained. Thioanisole was always recovered mixed with higher boiling fractions, which may contain alkylated thioanisoles (*cf.* Baddeley, 1944).

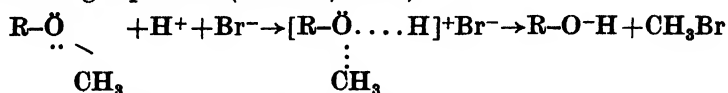
The stability of aliphatic sulphides to aluminium chloride has previously been noted by Lee and Dougherty (1939), who found that *n*-amyl sulphide was unaffected by two hours' refluxing with aluminium chloride in benzene solution. Auwers and Arndt (1909) were unable to demethylate 2-aceto-4-methyl thioanisole with aluminium chloride, but Harnish and Tarbell (1948) showed that the more labile phenyl benzyl sulphide gave 21% debenzylation when treated at 50° C. for twenty-four hours with the same reagent.

Alcoholic potash which demethylates anisole slowly at 200° C. had no appreciable effect on thioanisole after seven hours at 230° C.

Thus from the above and previous results (Hughes and Thompson, *loc. cit.*) it is obvious that thioanisole is much more resistant to both acidic and basic reagents than is anisole. The effects of the reagents used are shown in the following table.

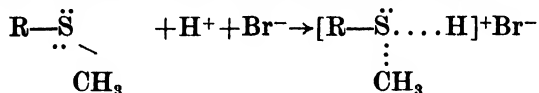
| Reagent. | Reaction Conditions. | Percentage Yield of Demethylated Product. | |
|-------------------------------------|----------------------|---|--------------|
| | | Anisole. | Thioanisole. |
| Hydriodic acid, hydrobromic acid .. | 2 hr. 130° C. | 100 | 0 |
| Pyridine hydrochloride | 6 hr. 200° C. | 100 | 0 |
| Magnesium iodide | 1 hr. 200° C. | 58 | 0 |
| Aluminium chloride | 2 hr. 100° C. | 100 | 20 |
| Caustic potash in ethanol | 7 hr. 200° C. | 7 | 0 |
| Sodium in pyridine | 5 hr. 120° C. | 94 | 62 |
| Sodium in ammonia | 7 hr. | 27 | 100 |
| | 15 hr. | (Birch, 1947) 100* | 100 |

The generally accepted mechanism for acid demethylation of ethers is shown in the following equation (Remick, 1942).



The proton addition is based on the well-known existence of H_3O^+ and $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{HCl}$.

However, the properties of divalent sulphur reveal that proton addition is extremely weak and the slight evidence for the existence of compounds such as $(\text{C}_2\text{H}_5)_2\text{S} \cdot \text{HCl}$ and H_3S^+ (Bagster, 1911; Jablczynska-Jedrzejewska and Groyecka, 1937) suggests that the analogous process

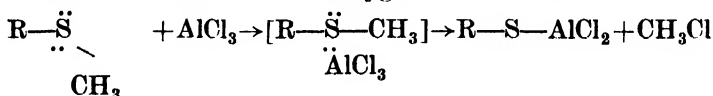


would be much less likely, and if this is the rate controlling step, then the reaction would be very slow. Furthermore, Fehnel and Carmack (1949) have presented evidence for the polarisation of the phenylmercapto group in which the benzene ring acts as an electron donor to the sulphur atom as shown in the following structures.

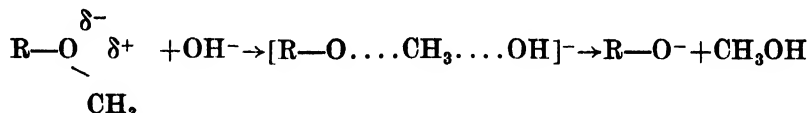


This would compensate for any loss of electron density on the sulphur atom (after the addition of the proton) and thus prevent the weakening of the sulphur carbon bond. Resonance involving these structures cannot occur with ethers as oxygen cannot expand its valency shell.

However, it is well known that sulphides co-ordinate readily with alkyl halides to form sulphonium salts while there is apparently no evidence for a similar reaction with ethers; sulphides also co-ordinate readily with oxygen to form sulphoxides and sulphones, and with halides of mercury and platinum metals, and it is reasonable to assume that this is why aluminium chloride will split thioethers, although here too the weakening of the sulphur-carbon bond is much less than is the case with the oxygen-carbon bond.



With alcoholic alkali the effective reagents must be the hydroxyl or ethoxyl ions which exert a nucleophilic attack on the carbon atom. The greater polarity of the carbon atom in anisole, due to the greater electron attracting power of oxygen, should make it more easily attacked, which is in accord with the experimental results.

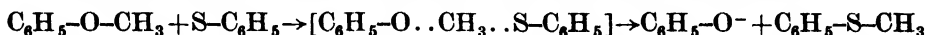


(If this is the mechanism for the alkaline hydrolysis it is difficult to understand why anisole metalates in the *ortho* position with butyl lithium, whereas thioanisole undergoes lateral metalation (Gilman and Webb, 1940)).

The difference in the stability of the sulphur and oxygen alkyl linkages suggested the possibility of the transfer of the methyl group from anisole to thiophenol. As expected, when anisole and thiophenol were heated in the presence of hydriodic acid no transfer occurred, the anisole being demethylated in the normal way.

However, in the presence of alcoholic potash the thiophenoxide ion caused complete demethylation of anisole after six hours' heating at 200° C. In the absence of thiophenol the yield of phenol under the same conditions was only 7%. Stoemer and Kahlert (1901) obtained 12% phenol after fifteen hours.

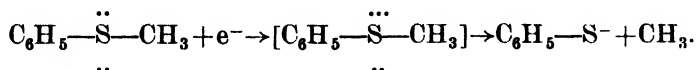
The reaction apparently involves a nucleophilic attack on the carbon atom and proceeds as follows because none of the otherwise expected intermediate products will methylate thiophenol under these conditions, and although the reaction was carried out in ethanol only thioanisole was obtained.



The reaction is applicable to methyl ethers other than anisole. Hexestrol and stilbestrol dimethyl ethers were both quantitatively demethylated in the presence of thiophenol and alcoholic potash after four hours heating at 200° C. Thioanisole was obtained as before and in the absence of thiophenol the yield of the phenols was very low. With stilbestrol dimethyl ether no addition of thiophenol across the double bond occurred. This is in agreement with the findings of Posner (1905), who under a variety of conditions could not obtain an addition product from thiophenol and stilbene.

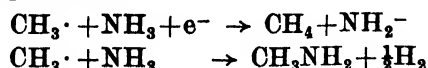
Although thioanisole is much more resistant to acidic and basic reagents than anisole, sodium in liquid ammonia, which rapidly and quantitatively splits thioanisole (Hughes and Thompson, 1948) has but a slow action on anisole (Birch, 1947; Hughes and Thompson, *loc. cit.*).

The mechanism for this reaction must therefore differ from those of the acid and basic reagents. Sodium in liquid ammonia behaves as a solution of metal cations and solvated electrons in equilibrium with metal atoms (Kraus, 1921) and consequently could be expected to react by electron addition. The ability of the sulphur atom to expand the number of electrons in its valency shell (oxygen cannot) would facilitate the formation of a transition state in the case of thioanisole.



With anisole the reaction is much slower, but quantitative. Thus we have found that increasing the reaction time from seven hours to fifteen hours increases the yield of phenol from 27% (Birch, *loc. cit.*) to 100%.

The formulation of the transition state by the addition of two electrons with the separation of two anions (Birch, *loc. cit.*) appears less likely than the addition of one electron followed by formation of the thiophenoxide ion and the free methyl radical. The latter would rapidly react with an ammoniated electron or an ammonia molecule to form methane and an amide ion, or methylamine and hydrogen respectively.



In a quantitative experiment Williams and Gebauer-Fuelnegg (1931) isolated ethane from the reaction between diethyl sulphide and sodium in liquid

ammonia and the yield of sodamide and ethane (approx. 75%) compared with the yield of sodium ethyl sulphide (95%) suggests that both these reactions may occur.

Kraus (1923) has noted the stability of aliphatic ethers to this reagent.

EXPERIMENTAL.

Demethylation of Thioanisole by Sodium in Pyridine.

To a stirred solution of thioanisole (12.4 g.) in refluxing dry pyridine (50 ml.) was added small pieces of sodium, the reaction being conducted in a stream of nitrogen. The solution rapidly turned purple and became progressively darker and more viscous.

After five hours the mixture was treated with aqueous pyridine to remove unreacted sodium, diluted with water and extracted with ether to remove any unchanged thioanisole.

The aqueous solution was acidified with hydrochloric acid and extracted with ether. The ether extracts after filtering to remove suspended matter were washed with water and dried over calcium chloride. Removal of the solvents by fractionation followed by distillation of the residue gave thiophenol (6.5 ml., 62% ; b.p. 169–172° C.).

No thioanisole was recovered from the ether extract of the acid solution.

Under the same conditions Prey (*loc. cit.*) isolated 94% phenol from anisole,

Demethylation of Thioanisole by Aluminium Chloride.

Thioanisole (10 g.) and powdered anhydrous aluminium chloride (11 g.) were heated on a water bath for periods ranging from two to seven hours. During this time the mixture darkened in colour and sulphur containing vapours were evolved which turned lead acetate paper black.

The mixture was poured on to ice, treated with hydrochloric acid and extracted with ether. The ether layer was extracted several times with caustic soda solution and the alkaline extracts acidified and extracted with ether. After washing and drying over calcium chloride both ether extracts were carefully distilled using a fractionating column (both thiophenol and thioanisole are appreciably volatile in ether).

The yields of thiophenol were usually low and thioanisole was recovered together with other neutral products of high boiling point.

The yield of thiophenol varied from 7% to 35% (b.p. 169–172° C.) and no other substance was isolated from the alkali-soluble fraction.

The amount of thioanisole recovered varied from 75% to 30% (b.p. 194–196 °C.)

The higher boiling fractions accounted for 10–20% of the original thioanisole, but no attempts were made to identify the substances present. Some solid substances crystallised from these fractions.

Heating the mixture at 120° C. caused considerable frothing, increased the quantity of sulphur-containing vapours evolved, and lowered the yield of thiophenol.

Thioanisole and Alcoholic Potash.

Thioanisole (12.4 g.) caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 230–235° C. for seven hours. The reaction mixture was poured into water and extracted with ether. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. After washing, drying and removal of the ether a negligible amount of oil remained.

Demethylation of Anisole by Thiophenol.

Anisole (10.8 g.), thiophenol (11 g.), caustic potash (8 g.) and alcohol (40 ml.) were heated in an autoclave at 200° C. for six hours. After cooling, water was added and the mixture extracted with ether. The ether extracts were washed with water, dried over calcium chloride and the ether fractionated off. Distillation of the residue gave only thioanisole b.p. 192–198 °C. (9.6 g.). The thioanisole was further characterised by oxidation of 2 g. in acetic acid solution with a solution of potassium permanganate (4.7 g.) in water (140 ml.). The solution was decolorised with sulphur dioxide and partially neutralised with caustic soda. The white

solid (2.2 g.) which separated was filtered off and after recrystallisation from methanol melted at 87° C. and did not depress the melting point of an authentic specimen of the sulphone of thioanisole.

The alkaline solution was acidified, extracted with ether, and the ether extracts washed and dried. Removal of the ether followed by distillation gave phenol (8 g.) b.p. 182–185° C.

In a parallel experiment in which the thiophenol was omitted only 0.6 g. phenol (7%) was obtained.

Substitution of water (30 ml.) for the alcohol gave phenol (8 g.). When the reaction was carried out at 180° C. for six hours only 45% phenol was obtained, while at 150–170° C. for 24 hours 58% phenol was isolated.

Attempts were made to carry out the reaction at atmospheric pressure by refluxing with ethylene glycol or glycerol but after 18 hours no transfer of the methyl group had occurred. The reflux temperature in these experiments was only about 150° C.

Diphenyl ether was substituted for anisole in one experiment but no transfer occurred.

Demethylation of Hexestrol Dimethyl Ether and Stilbestrol Dimethyl Ester by Thiophenol.

The ether (1.5 g.), caustic potash (1.5 g.), thiophenol (2 ml.) and alcohol (20 ml.) were heated together in an autoclave at 200–210° C. for four hours. Water was added on cooling and the mixture extracted with ether.

The alkaline solution was acidified, boiled for several minutes to remove the volatile unchanged thiophenol and cooled.

The solid which separated was dried and recrystallised from benzene.

From hexestrol dimethyl ether was obtained hexestrol (1.35 g.) m.p. 184° C. It did not depress the melting point of an authentic specimen of hexestrol.

From stilbestrol methyl ether stilbestrol (1.35 g.) m.p. 169° C. was obtained, which was identified by mixed melting point.

The thioanisole isolated from the original ether extract was steam distilled and oxidised as before to the sulphone m.p. and mixed m.p. 87° C.

Parallel experiments in which the thiophenol was omitted gave only very small yields of the phenols.

Demethylation of Anisole by Sodium in Liquid Ammonia.

Anisole (9 g.) was added to ammonia (200 ml.) containing sodium (9 g.), with stirring during 15 minutes, in a flask surrounded by liquid ammonia contained in a Dewar flask. After standing 15 hours the ammonia was allowed to evaporate and crushed ice (100 g.) added as rapidly as was safe. The mixture was extracted with ether, the ammonia boiled from the aqueous solution, which was then acidified.

The phenol was extracted with ether (4 × 50 ml.), the solution dried, the ether removed and the phenol (7.5 g.) b.p. 181–183° C. distilled. No anisole was recovered from the ether solution.

In a similar experiment using sodium (6 g.) Birch (*loc. cit.*) obtained 27% phenol after seven hours.

ACKNOWLEDGEMENTS.

The authors are indebted to Andrews Laboratories for samples of hexestrol, stilbestrol and their dimethyl ethers; and to Dr. S. Angyal for helpful discussions.

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ACTION OF PHOTOCHEMICALLY PRODUCED RADICALS ON ACETYLENE.

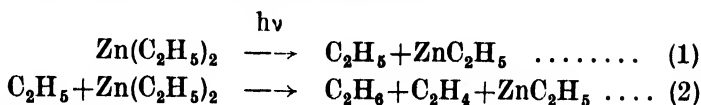
By L. E. LYONS, B.A., M.Sc.

University of Sydney.

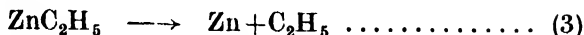
Manuscript received, November 3, 1949. Read, December 7, 1949.

INTRODUCTION.

The photodecomposition of zinc diethyl has been studied by Moore and Taylor (1940), who postulated the following reactions :



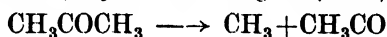
together, presumably, with



Evidence presented in this paper supports this mechanism.

It is to be noted that reaction (1) involves the liberation of free ethyl radicals from the zinc diethyl molecule, a process which must take place within one vibration period as there is a continuum in the ultra-violet absorption spectrum of zinc diethyl below 280 m μ (Thompson (1935) and Thompson and Linnett (1936)).

Now there is evidence that gaseous acetylene can be polymerised even at room temperature by the action of free radicals, e.g. by methyl radicals formed in the photolysis of acetone (Taylor and Jungers (1937)).



this phenomenon has been observed in the course of these experiments also.

Thus there was good reason to expect that the photolysis of zinc diethyl in the vapour phase would induce polymerisation of gaseous acetylene. The study of this reaction is now reported.

EXPERIMENTAL.

The apparatus is illustrated in Fig. 1.

The lamp, shown at left in Fig. 1, was a high-pressure type, the discharge taking place in an inverted U-tube. The 253.7 line was reversed.

The effect of light on acetylene itself was one possible complication. The photopolymerisation of this substance has been studied by Lind and Livingstone (1930), who found a quantum yield of nine at 215 m μ . Wave-lengths much higher than this are not absorbed. Therefore, using the full light of our quartz mercury lamp, which had only a slight output in the active range, only a slight direct photopolymerisation was to be expected. Tests showed that this was negligible for our purposes.

The pressure gauge was an ordinary mercury manometer.

The presence of mercury vapour did not affect the reaction because of the absence of the 253.7 m μ line. A trap included in the line served to hold the distilled zinc diethyl before volatilisation into the reaction vessel. A Töpler

pump was used to collect product gases. The *zinc diethyl* was prepared and purified according to the method of "Organic Syntheses". It was stored in the dark and separated from the rest of the apparatus by two stopcocks. *Acetylene* was obtained from a cylinder and passed through sodium bisulphite and sodium hydroxide solutions and a dehydrating chain. It was also frozen and revolatilised three times, with appropriate evacuation of the last fraction each time, before being stored in a bulb. *Acetone* was purified by the method of Weissberger and Proskauer (1935), distilled into the trap, and then admitted to the reaction vessel. During a run the reaction vessel was shut off from all but the pressure gauge. Room *temperature* conditions were held by a stream of water over the outside of the reaction vessel. A *zinc film* appeared on the inside wall nearest

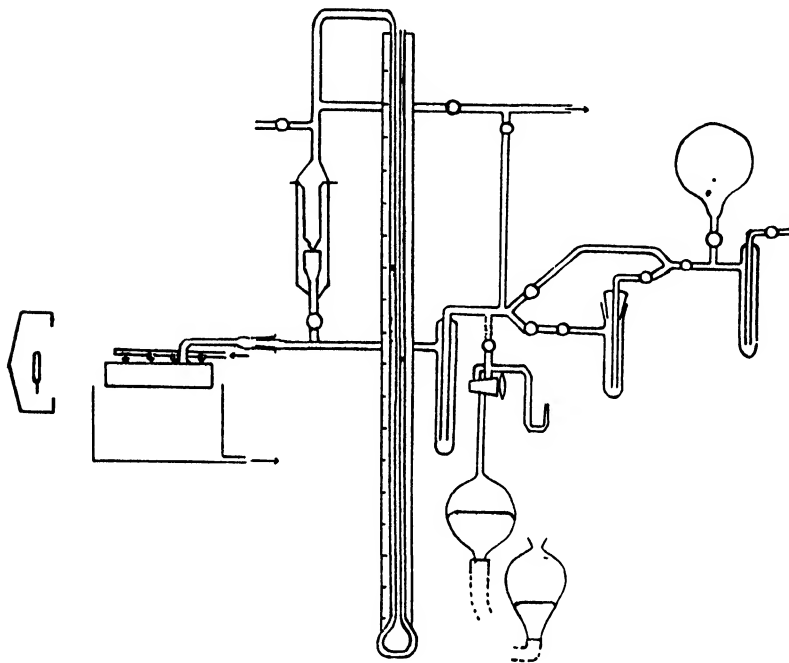


Fig. 1.

the light when zinc diethyl was used. This was estimated at the end of a run as follows: The zinc was dissolved in dilute sulphuric acid and the volume made up to 100 ml. Ten millilitres of this were made just alkaline with dilute ammonia, extracted with dithizone solution in redistilled chloroform. The chloroform extract was washed with ammonia and made up to 25 ml. This red solution was compared in a "Spekker" photoelectric colorimeter with similar preparations made from standard zinc sulphate solutions.

RESULTS.

(1) A film of polymer appeared on the inside of the reaction vessel whenever zinc diethyl or acetone was present with acetylene. The polymer was light-brown in colour and resembled cuprene. It was stable to heat in a vacuum. It was insoluble in ordinary organic solvents and also in concentrated nitric acid. Examination with a polarising microscope showed it to be slightly birefringent, but X-ray photographs both of a flake and of a powder made from it showed no sign of a crystal structure.

(2) Irradiation of an acetone-acetylene mixture gave results shown in Table I.

(3) Irradiation of zinc diethyl, acetylene and mixtures of the two gave results which are summarised in Table II.

In the table, results in lines 2, 3, 4, 5, 8 and 10 are all based upon independent experimental measurement. Figures in lines 6, 7 and 11 are deduced from the others. Figures in line 10 are calculated from the amount of metallic zinc deposited and found by analysis.

TABLE I.
Acetone-Acetylene.
Time of irradiation: 1130 mins. Temperature: 22° C.

| | Initial Pressure. (Mm.) | Final Pressure. (Mm.) |
|--------------------|----------------------------|--------------------------|
| Acetylene | 137 | — |
| Acetone | 188 | — |
| Carbon monoxide .. | — | 8.3 (by analysis) |
| Total | 325 | 318 |

TABLE II.
Zinc Diethyl, Acetylene.
Temperature: 22° C. \pm 2. Pressures in mm. mercury.

| 1 | Run | 11 | 13 | 14 | 15 | 16 | 17 |
|----|---|------|-----|-------|-------|-----|------|
| 2 | Time (mins.) | 117 | 135 | 40 | 82 | 81 | 153 |
| 3 | Zn(C ₂ H ₅) ₂ , initial | 19 | 0 | 20 | 20 | 16 | 14.5 |
| 4 | C ₂ H ₂ , initial | 0 | 282 | 215.5 | 142 | 0 | 325 |
| 5 | Total, final | 21.5 | 281 | 239 | 163 | 19 | 342 |
| 6 | Zn(C ₂ H ₅) ₂ + C ₂ H ₂ , final | — | — | 206 | 142 | — | 318 |
| 7 | Zn(C ₂ H ₅) ₂ , final | — | — | — | 16.8 | 19 | 10 |
| 8 | C ₂ H ₂ , final | — | — | — | 125.5 | — | 308 |
| 9 | Product gases | — | — | 44 | 21 | 5.7 | 24 |
| 10 | Decrease in Zn(C ₂ H ₅) ₂ | — | — | — | 3.2 | 2.7 | 4.5 |
| 11 | Decrease in C ₂ H ₂ | — | — | — | 16.5 | — | 17 |

Notes.

Run 12 discarded as analysis revealed acetylene to be impure.

Runs 1–10 were made with an insufficiently accurate manometer and were discarded.

DISCUSSION OF RESULTS.

(1) The efficiency of the free radicals from acetone in polymerising acetylene may be estimated as follows:

One molecule of carbon monoxide is formed from one molecule of acetone so that a measure of the acetone decomposed is possible. After allowing for the carbon monoxide present in the final mixture, the decrease in total pressure which was observed is a direct measure of the acetylene polymerised, since one molecule of acetone gives rise to one molecule of ethane besides the carbon monoxide. Biacetyl is not formed in the presence of a foreign gas (Iredale and Lyons (1944)).

Let $p_{0,f}$ denote the original, final pressure, and

p_{CO} ,, ,, carbon monoxide pressure.

Then number of molecules of acetylene polymerised for each free radical

$$\text{produced} = \frac{P_0 - P_1 + P_{CO}}{P_{CO}}$$

$$= \frac{325 - 318 + 8}{8}$$

$$= 1.9 \text{ molecules/radical.}$$

This agrees with the results of Taylor and Jungers (1937).

(2) The photolysis of zinc diethyl is known to give no butane at room temperatures, but only ethylene and ethane, i.e. one molecule of zinc diethyl gives two molecules of products (Moore and Taylor (1940)).

From Table II, run 16, it is seen that one molecule of zinc diethyl does give 2.1 moles of products, and so the earlier work is confirmed.

(3) In the runs where acetylene was present with the zinc diethyl, the results indicate the formation of vapour products other than from the zinc diethyl, e.g. in run 15 there were 6.7 moles of products for one mole of zinc diethyl used, and in run 17, 5.3 moles of products. The gaseous products were in every case completely condensable with liquid air, indicating that neither hydrogen nor methane was present.

As the only possible source of gaseous products apart from the zinc diethyl was the acetylene itself, it is concluded that the reaction produces from the acetylene (a) a volatile compound as well as (b) a solid polymer.

(4) The ethyl radical polymerisation efficiency may be calculated by saying that :

Number of radicals produced = $2 \times$ number of molecules of zinc diethyl decomposed.

The results give 2.5 molecules polymerised/radical for run 15, .

and 1.9 molecules polymerised/radical for run 17.

These figures may be compared with 1.9 molecules/methyl radical (see above) for acetone-acetylene, a figure obtained by a totally different method. Thus it may be said that methyl and ethyl radicals are of about equal efficiency in polymerising acetylene.

(5) The percentage of ethyl radicals efficient in producing polymerisation may be calculated assuming a mean number of C_2 units in the polymer.

For three units in the polymer, 75 % of the radicals are effective polymerising agents, for four units 55 % and for six, 37 %. So it is seen that about one in every two radicals initiates a chain.

SUMMARY.

(1) Zinc diethyl photolysis involves free radicals and the previously postulated mechanism is supported.

(2) Acetylene is polymerised by methyl and ethyl radicals with about equal efficiency.

(3) The products of the polymerisation are (a) a volatile substance, and (b) a non-crystalline solid.

(4) 2.2 molecules of acetylene polymerise for each radical produced.

(5) One in every two radicals initiates a chain.

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A FURTHER CONTRIBUTION TO THE GEOLOGY OF THE GOULBURN DISTRICT, N.S.W.

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Manuscript received, October 19, 1949. Read, December 7, 1949.

PART I. EVIDENCE OF A MAJOR FOLD-STRUCTURE IN THE PALÆOZOIC ROCKS TO THE EAST OF GOULBURN.

In a paper published in this journal in 1935 (Naylor, 1935) the writer expressed the opinion that certain observed relationships between Silurian and Ordovician strata near Bungonia could best be explained by the assumption of an overfolded structure.

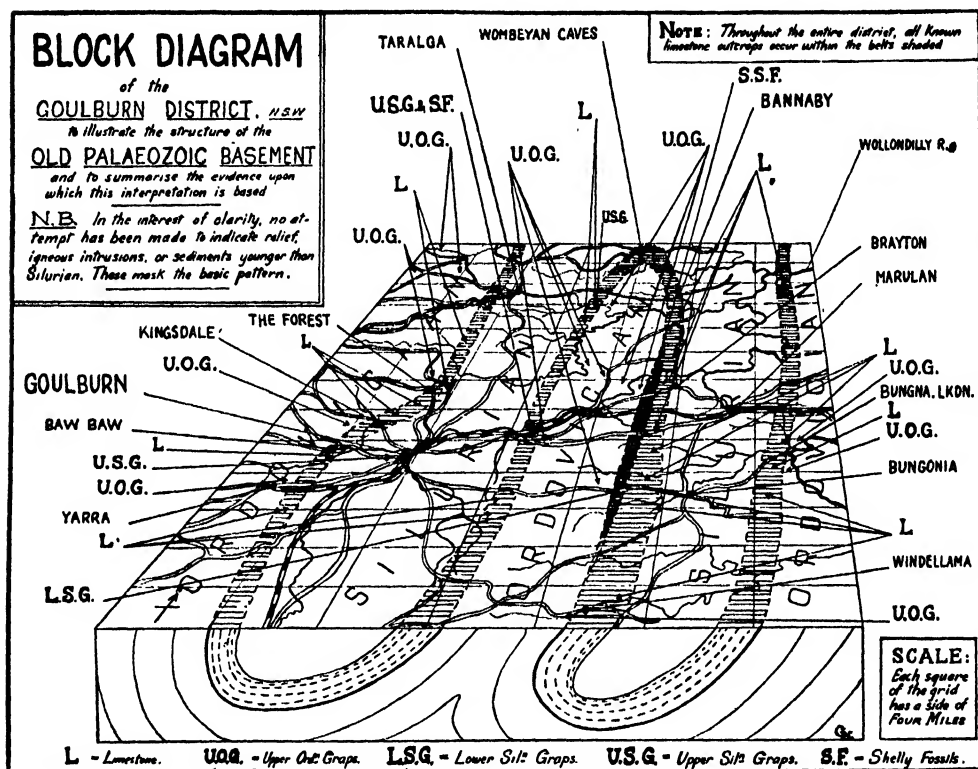
This seemed to afford the best suggestion to account for the fact that rocks with a definite Upper Ordovician graptolite fauna overlie (in the field) other strata with equally definite Lower Silurian graptolites. The evidence for the fold structure was then admittedly incomplete; but shortly after the publication of the paper mentioned additional field work enabled many of the gaps to be filled in. The writer was preparing a further communication on this matter in 1939, but was interrupted by the war. No more field work was possible until 1945, and this tended to confirm the evidence for the fold structure, while bringing to light certain unexpected facts which render necessary a complete review of the Palæozoic sequence near Goulburn itself. It was the intention of the writer to carry out the field work necessary to attempt this review, and to publish the additional evidence for the fold structure at the same time. Since his appointment to the staff of the University of Queensland in 1946 no opportunity to renew field work at Goulburn has occurred, and may not do so for some time. Hence this opportunity is being taken to present the data at present available, for the benefit of other workers in adjoining areas. A brief mention will also be made of the evidence which appears to preclude the acceptance of the Upper Devonian age that has been traditionally assigned to the rocks in the immediate vicinity of Goulburn.

Summary of Observations Previously Recorded.

On the road section between Bungonia and Goulburn were noted rocks of Upper Ordovician age. These dipped steeply to the west and apparently overlay strata containing a Lower Silurian graptolite fauna, also dipping to the west. These in turn appeared to overlie a series of slates and quartzites including isolated patches of limestone, which were assumed, in the absence of evidence to the contrary, to be of Upper Silurian age. There was thus an apparent inversion of these three series, suggesting that they occupied the underlying limb of a great anticlinal fold, overturned towards the east. It was assumed that the Upper Silurian Series east of Bungonia represented the eastern limb of an adjacent syncline. It was further inferred from the presence of Silurian graptolites on the Marulan-Goulburn road section, that Silurian rocks were present on the western limb of the anticline, adjacent to the western boundary of the Ordovician belt. The assumed structure was indicated in a sketch section published along with the paper.

Additional Evidence from Bungonia-Goulburn Section.

(a) In a paper written in 1936, Garretty (1936), while agreeing generally with the structure offered above, suggested that the limestones in portions 18 and 46 ph. Jerrara, might be of Devonian rather than Silurian age, as previously assumed by the present writer. A more recent examination, however, has revealed that a bed of limestone, not outcropping at the surface, has been met in a shaft sunk a little to the north of the outcrop in portion 18. Amongst the blocks of limestone which had unquestionably been removed from the shaft and hence may be regarded as being *in situ*, were found good specimens of *Pentamerus knighti*, supporting the assumption of an Upper Silurian age for this limestone belt.



More convincing evidence of the pre-Devonian age of the limestones lies in the fact that they are metamorphosed by the Marulan batholith, while the known Devonian lies upon its eroded surface (Naylor, 1939).

(b) Thanks to information supplied by a local resident, Mr. I. Frost, limestone has been located and examined by the writer in two adjacent localities to the west of the Ordovician belt along the course of McKellar's Creek, about six miles east of Goulburn. The two outcrops of limestone occurring here do not appear to have been recorded by Carne and Jones in their survey. They are small in extent and of no economic significance. Both outcrops are marmorised by the contact effects of the adjacent porphyritic rocks, but contain numerous fossils, mainly tabulate and rugose corals, an assemblage corresponding to that of the Silurian limestones elsewhere. *Favosites* and *Heliolites* are recognisable generically but the species are indeterminate.

(c) A series of relatively soft light-bluish-grey clay-stones are met immediately to the west of the limestones on the eastern side of the Ordovician belt. From this, however, they are separated by the Lower Silurian shales of the Jerrara Beds, and hence they must be assigned to the Silurian group. Whether they should be classed as Upper or Lower Silurian is a matter of doubt, since they themselves appear to contain no fossils. However, what is presumably the same horizon has been located a little to the east of the McKellar's Creek limestone, adding to the symmetry of the distribution of the strata, and lending support to the assumption of an anticlinal fold. Additional confirmatory evidence in favour of this interpretation is offered by the distribution of the quartzitic horizon of the Silurian series.

(d) The Upper Ordovician rocks themselves show a similar tendency towards symmetrical distribution of characteristic horizons, while a zone towards the central part of the belt shows evidence of great compressive stresses such as might be expected to occur along the axis of a fold some distance below the original surface.

The corresponding rock zones on either side of this supposed axis tend to be wider to the west than to the east. However, this would appear to agree well with the conception of an over-fold in which it is reasonable to expect the upper (here western) limb to be thickened by compression, while the thickness of the lower (eastern) limb would be reduced by tension.

Evidence from the Marulan-Goulburn Section.

Proceeding west from Marulan the igneous rock is found to extend for about a mile and a half beyond the Bungonia turn-off, after which one meets relatively gently dipping quartzites and sandy shales (dip W. at 30° – 40°). These may be of Upper Devonian age and consequently not immediately connected with the problem of the Ordovician and Silurian folding. However, this should not be too readily assumed. Further on, the dip of the strata is found to be steeper, reaching the 50° – 80° range characteristic of the older Palæozoic rocks. Lithologically the rocks here consist of quartzites with thin interbedded bands of slate and claystone, the colour and texture of both being characteristic of those associated with the Silurian elsewhere. Just before reaching Shelley's Flat, a thick series of soft bluish-grey claystones, almost devoid of quartzites, occurs. On the eastern edge of these shales, just opposite the residence of Mr. Henderson, to whom the writer is indebted for the information, is a very small outcrop of what is probably a larger underlying mass of limestone. The small amount of limestone that is exposed is quite fossiliferous, the types including tabulate and rugose corals, not well enough preserved for specific identification.

Another small outcrop of limestone, which more closely approaches a travertine, occurs about a mile to the south, but is probably of secondary origin and hence of little immediate structural significance.

Occupying the "Flat" itself, and largely masked by alluvium, is a series of slates which seem to correspond with the Jerrara Beds, though graptolites have not been found in them in this locality. (It should be pointed out that the extent of the Jerrara series has been investigated further since the writer's earlier paper, and is now known to be at least four miles along the strike, having been traced on either side of the Bungonia-Goulburn road as far south as Bungonia Creek and as far north as Jerrara Creek. A continuation of this line would intersect the Hume Highway very close to Shelley's Flat, and pass northward a little to the west of Brayton.)

From the western edge of the Flat almost to the Carrick turn-off, a distance of about five miles, one passes over graptolite-bearing rocks of Upper Ordovician age. These are lithologically distinct from the Silurian types. Well cleaved

bluish-grey slates, quartz schists, and blue cherts predominate. The slates are much harder than those of the Silurian, especially of the Upper Silurian.

Graptolites are plentiful towards the margins, though occasionally their collection is rendered difficult by the development of cross-cleavage. A small collection taken from the Carrick Road on the western margin was submitted some years ago to Dr. D. E. Thomas, who identified the forms as belonging to an extreme Upper Ordovician horizon.

A much more extensive collection has now been made by the author from cuttings in more recently constructed deviations in the Hume Highway. Two horizons in which graptolites are particularly abundant occur on the western and eastern margins of the Ordovician belt. The graptolites in these two localities are quite well preserved, and the similarity of the assemblages shown below would appear to suggest beyond reasonable doubt that the same horizon is represented in both cases. The extreme Upper Ordovician age of this horizon is also indicated.

(a) *Forms occurring in the Western Locality.*

Dicellograptus sp.
Diplograptus truncatus.
Diplograptus quadrimucronatus var.
spingerus.

Climacograptus cf. *rectangularis*.
Climacograptus sp.
Leptograptus cf. *capillaris*.
Diplograptus cf. *calcaratus*.
Diplograptus calcaratus var. *tenuicornis*.

(b) *Forms occurring in the Eastern Locality.*

Climacograptus rectangularis.
Climacograptus supernus.
Climacograptus sp. (other than above)
Diplograptus sp.
Retiograptus cf. *pulcherrimus*.
Dicellograptus pumilus.
Dicellograptus cf. *forchhammeri*.

About 200 yards east of the Carrick Road Junction, the Ordovician strata give place to soft greyish-blue shales containing *Pentamerus knighti* and other shelly fossils, as well as recognisable *M. bohemicus*. Another hundred yards to the west are finely banded bluish-grey shales containing Upper Silurian graptolite forms (Naylor, 1935a). These shales, with interbedded quartzite, can be traced onward as far as Boxer's Creek, where they are terminated by a porphyritic intrusion about half a mile in width. Thereafter the slates continue to the foot of Governor's Hill, where there is no clear boundary between these and the arenaceous rocks that have hitherto been accepted as Upper Devonian. It can be seen from this description that the main features of the section along the Hume Highway are very similar to those of the section along the Bungonia-Goulburn road, a distance of four to six miles further south.

Evidence from an East-West Section through Brayton.

The sedimentary rocks to the north and west of Brayton are separated from those just described by a westward projection of the Marulan batholith, but corresponding types are found and there is no doubt of their original continuity with those of the areas just described. The relation between the Silurian and Ordovician strata near Brayton which puzzled the writer for many years becomes simplified in the light of the folding deduced from observations further south.

Adjoining the porphyritic complex near Brayton Cross-roads is an outcrop of marmorised limestone, to the west of which are hornfelses and metamorphosed tuffs, together with interbedded flows of lamprophyre. This region appears to have been a volcanic centre in Silurian times, but most of the metamorphism is

probably due to the proximity of the batholith. What may be called the "volcanic" series can be traced westward for about a mile and is succeeded first by quartzites then by a thick series of slates with very little quartzite. These extend for fully half a mile, until finally there is exposed in a creek bed a highly silicified rock containing numerous Silurian shelly fossils, in which the genus *Atrypa* predominates. (These were identified as definitely Silurian by the late Mr. Chapman.) Fifty yards beyond this point the lithology changes and the characteristic hard, cleaved, bluish-grey slates and cherts of the Ordovician series outcrop.

All the rocks here are dipping to the westward, so that the Silurian appears to underlie the Ordovician, an impression which is greatly strengthened by the fact that the fossiliferous bands on the edge of the Silurian outcrop in the creek bed, while Ordovician graptolites may be collected high above them on the hillsides.

The exact age of the Silurian rocks here is doubtful. It may be assumed with reasonable safety that the Brayton limestone is Upper Silurian, since this age has been proved for most of the limestones in this district. It is highly marmorised and fossils are very scarce. The writer is inclined to the opinion, based on lithological similarity, that the western portion of the slates corresponds to the Jerrara series and hence is of Lower Silurian age. This would imply that the fossiliferous beds adjacent to the Ordovician are also Lower Silurian—an assumption which the fossils themselves do not appear to either confirm or deny. While undoubtedly Silurian types, their exact horizon is so far indeterminate.

The Ordovician beds nearest the Silurian contain fairly well preserved graptolites, and would appear to represent the uppermost part of the Upper Ordovician system. The following forms have been collected:

Climacograptus bicornis.

Diplograptus quadrimucronatus.

Dicellograptus complanatus.

West of Brayton the Ordovician belt extends for about four miles to the foot of the main Cookbundoon Range, where it is unconformably overlain by the marine sediments of the Upper Devonian. Graptolites are fairly numerous throughout this region of Ordovician rocks, but there are certain marked changes in the distribution of the forms which have a distinct bearing on the present problem.

As has been pointed out, the eastern margin appears to be of very late Ordovician age. About two miles further west, however, near the Greenwich Park-Towrang Road, occur numerous graptolites of a distinctive and diminutive nature which were regarded by Dr. Thomas as being representative of the lowest part of the Upper Ordovician, and the writer's own observations seem to point to the same conclusion. The list of forms identified by Dr. Thomas are as follows:

Dicellograptus sextans.

Cryptograptus tricornis.

Dicellograptus divaricatus var. *augustus* (nov.).

cf. *Leptograptus*.

Diplograptus sp.

Further west again the fauna appear to belong to a higher zone:

Dicellograptus elegans.

Climacograptus cf. *caudatus*.

Dicranograptus hians var. *apertus*.

For these identifications the writer is also indebted to Dr. Thomas.

In this line of section one cannot inspect the western junction between Ordovician and Silurian series since it is overlain by the Devonian strata. However, in the same line, beyond the Cookbundoon Range, the Silurian limestones of The Forest are situated a little to the east of another graptolite-bearing Ordovician belt.

*Evidence from the Section near Kerrawary Creek and the
Cookbundoon River.*

The information so far available concerning this section is not very detailed but is significant when considered in conjunction with the other sections just described.

North of Big Hill, on the southern bank of the Cookbundoon River, about two miles west of the Swallow-tail Pass, there occurs an isolated outcrop of marmorised limestone extending discontinuously for about a quarter of a mile along the western margin of the igneous intrusion that occupies so much of the country in that vicinity. No fossils other than crinoids have survived the metamorphism to which this limestone has been subjected, but its alignment corresponds to that of the Bungonia-Brayton limestone belt, and supports the assumption of its Silurian age. Further west, near the junction of the River with Kerrawary Creek, occur graptolites which are definitely Upper Ordovician types, though an exact list of forms is not available. A collection made by the writer from the western portion of this belt between Kerrawary Creek and the Bannaby-Taralga road includes the following types:

Diplograptus calcaratus.

Dicellograptus cf. *complanatus.*

Dicellograptus complanatus var. *ornatus.*

Dicranograptus clingani.

Still further westward near the junction of Kerrawary Creek and Cowhorn Gully, there is a prominent outcrop of fossiliferous Upper Silurian limestone with interbedded shales containing *Monograptus*. These have already been noted by the writer (Naylor, 1937). West of Taralga Upper Ordovician graptolites have been collected at numerous localities in the vicinity of Goldspie and Yalbraith, and at Bumaroo Ford.

Summary of Evidence.

It is readily admitted that the data available in any single one of these sections is, for various reasons, incomplete; but considering the evidence as a whole the conclusion that there is a major overfolded anticlinal structure in the Ordovician and Silurian rocks appears to be inescapable. What is lacking in one section is supplied from a parallel one. Thus the absence of graptolites on the western part of the Bungonia-Goulburn Section is compensated by their abundance on the corresponding part of the Marulan-Goulburn Section, where the boundary between Ordovician and Silurian strata is well defined. Similarly the absence of Upper Silurian limestone from this part of the latter section is offset by the occurrence in McKellar's Creek. The lamprophyres and breccias characteristic of the Silurian series at Brayton may or may not occur beneath the Devonian strata to the west of the Ordovician belt, but they certainly have a counterpart in the western Silurian belt between the Bungonia-Goulburn and Marulan-Goulburn roads.

Stratigraphical Implications.

Certain inferences concerning the sequence and relationship of the older Palæozoic rocks may be drawn from the foregoing discussion. In the first place it would appear that the structures present are fundamentally simpler than had previously been supposed. An anticline rather than an anticlinorium

is suggested. It is true that much local folding may be observed throughout the area but this has never been traced for any appreciable distance. Moreover such folding appears to be confined to the more argillaceous sediments and may readily be attributed to "drag folding" caused by differential movement of more competent arenaceous beds on either side. These latter, as far as the writer is aware, exhibit only simple though steep dips.

If one accepts the existence of a huge and relatively simple anticline, to which the existing evidence tends to point, the folding of both Upper Ordovician and Silurian strata would appear to have resulted from the one movement. In other words the two series seem to be substantially conformable throughout. This view is supported by field evidence, since not only do both series appear to have suffered the same degree of folding, but where the junction between them can be located, no significant angular variation in the strike or dip has been observed.

Woolnough (1909), in the original paper on the Tallong-Marulan district, described an unconformity beneath the Upper Silurian limestone at Marulan, and the position of this structure has since been located exactly by Dr. G. D. Osborne. Geological opinion concerning the relations between Ordovician and Silurian in N.S.W. appears to have been considerably influenced by this occurrence, but the writer feels that it would be inadvisable to attach too much stratigraphical or structural significance to the angular nature of the exposed junction between the Marulan limestone and the underlying slates. In this locality the limestone is hundreds of feet in thickness and must have offered great resistance during the folding processes, with an almost inevitable disturbance of the original relationship between it and the adjoining less competent argillaceous beds. Moreover, the beds immediately below the limestone have never been proved to be of Ordovician age. This has merely been inferred from the assumption of unconformable relations. The writer, who has examined this locality, considers that the slates present the lithological characteristics suggestive of Silurian rather than Ordovician types, and it is significant that in no other locality have the limestones been shown to be the basal member of the Silurian series. Finally, angular discordance may be observed from Bungonia Lookdown between the base of the Upper Belt of limestone and the (presumably argillaceous) rocks which separate it from the Lower Belt.

In short, the bulk of the evidence at present available from the Bungonia-Goulburn district seems to indicate the absence of any appreciable epi-Ordovician orogeny, though the transition in many places from Upper Ordovician to Upper Silurian strata certainly implies a discontinuity of sedimentation.

Epi-Silurian folding, however, must have taken place on a grand scale, affecting both Upper Ordovician and Silurian strata, producing between Marulan and Goulburn a huge anticline which was overturned to the east. During this folding the Ordovician rocks, being more deeply buried, suffered a greater degree of dynamic metamorphism than the overlying Silurian strata. It is suggested that this accounts for the fact that the former exhibit a greater degree of recrystallisation and a more disturbed character than the latter, though the general dips of both series are equally steep.

An exception to the steep dips of the Silurian strata occurs in the immediate vicinity of Goulburn itself, where the competent nature of a large mass of quartzite appears to have exerted considerable resistance to the folding and resulted in shallower local dips (see Part II).

PART II. EVIDENCE CONCERNING THE AGE OF THE SEDIMENTARY ROCKS AT GOULBURN.

Those responsible for compiling the State Geological Map must have had some reason for assigning a Devonian age to a large area of country surrounding

the City of Goulburn and extending eastwards towards the Shoalhaven River. In view of the fact that the great bulk of this region has now been shown conclusively to be either Ordovician or Silurian, it is difficult to be certain what the basis of the earlier classification was. As far as the writer is aware from enquiries of the personnel of the Geological Survey, the provisional assignment of a Devonian age to these rocks was largely influenced by the collection of *Lepidodendron australe* and some marine fossils with strong Lambian affinities on the summit of the Cookbundoon Range. No doubt the lithological characters of the white quartzite of the Memorial Hill and the associated conglomerates and red beds further suggested that these rocks should be regarded as Devonian.

This view was absorbed by the writer as a student and never seriously questioned by him (or as far as he is aware, by anyone else) until quite recently. However, a careful examination of the actual state of knowledge on this matter has served to convince the writer that the following are the facts of the case :

- (a) The finding of *Lepidodendron australe* and the Lambian marine assemblage on the Cookbundoon Range at several localities has been confirmed personally by the writer's own collection of these forms at points along the whole length of the Cookbundoon Range from Narrangaril Trig. Station to the vicinity of Bannaby.
- (b) Similar marine Upper Devonian fossils occur in arenaceous beds along the course of Bungonia Creek, near Bungonia. (These are the beds which have been shown by the writer (Naylor, 1939) to lie upon the eroded surface of the Marulan batholith.)
- (c) No Devonian fossils have been found closer to Goulburn than those at Narrangaril Trig.—about five or six miles N.E. of the centre of the city.
- (d) There is no record of any collection of recognisable fossils from any of the quartzites, conglomerates or shales of the Memorial Hill, Governor's Hill or the immediate surroundings. The writer has literally spent weeks in a fruitless search for fossils in these rocks.
- (e) The continuity which has always been assumed to exist between the Memorial Hill quartzites and those of the Cookbundoon Range is by no means evident when one inspects aerial photographs of this region. The strike of the undoubted Upper Devonian (fossiliferous) beds of the Narrangaril locality is seen to sweep round to the westward without crossing the Wollondilly River or the main railway line, assuming a direction almost at right angles to the trend of the great whale-back of quartzite that extends for a couple of miles N.N.E. of the big Railway Department quarry at North Goulburn. Large alluvial flats at the bend of the river obscure the actual relationships of these two rock masses at what would appear to be their point of junction.
- (f) The discontinuity suggested by the aerial photographs is supported by field inspection of the critical area on the ground. Discontinuity can hardly be proved, but seems to constitute a more reasonable assumption than continuity. Whether there is or is not continuity (i.e. with or without conformity) the field evidence leaves no doubt that the Narrangaril beds would certainly overlie the Goulburn quartzites if they did all form part of the one series.
- (g) The quartzites outcropping in the North Goulburn Railway quarry are associated with bands of something akin to a quartz schist, in which carbonaceous fragments suggestive of organic remains are here and there abundant. The late Dr. F. A. Singleton, on viewing specimens of these, unhesitatingly proclaimed them to be graptolitic. However,

the writer himself is not prepared to make this claim, as he has been unable to distinguish any signs of graptolitic structure to his own satisfaction. Nevertheless, he has collected exactly similar specimens from the point of view of lithology and carbonaceous content at points north of Murray's Flats, where the sediments underlie the Narrangaril beds, and appear to be unconformably separated from them.

- (h) A careful examination, which the writer has been enabled to carry out many times, of an east-west section from the Memorial Hill through the City of Goulburn to and beyond the water storage tanks on the top of the hill to the west of the city, leads to the conclusion that the Memorial quartzite underlies the shaly and sandy beds on which the city itself is mainly built. These are folded into a syncline whose nearly meridional axis lies slightly west of the city.
- (i) In May 1945 the writer was fortunate enough to locate a horizon within this syncline where *Monograptus bohemicus* was abundant and easily recognisable.

CONCLUSION.

This would appear to justify the assumption of an Upper Silurian age for the beds of the Goulburn Syncline.

While the above facts do not provide positive evidence of the exact age of the Memorial Quartzite and its associated conglomerates, it seems unlikely that they are younger than Upper Silurian. The dips of these rocks would appear to be shallow in contrast with those of the Silurian elsewhere in the Goulburn district—a fact which has no doubt contributed to the general impression of their Devonian age. However, the beds in which *Monograptus* was collected are themselves dipping gently (E. 20° S. at 30°) and in any case the Yass district provides an example of a region where the folding of the Silurian strata has been comparatively gentle over a localised area.

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THE KUTTUNG VULCANICITY OF THE HUNTER-KARUAH DISTRICT, WITH SPECIAL REFERENCE TO THE OCCURRENCE OF IGNIMBRITES.

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INTRODUCTION.

The Kuttung Series in N.S.W. occupies the time interval from the top of the Tournaisian (mid-Lower Carboniferous) to the base of the Permian System. Thus it is to be regarded as the upper part of the Carboniferous in this State, although the flora of the Series suggests a correlation with the Middle Carboniferous of the Northern Hemisphere rather than with the Upper Carboniferous (Walkom, 1919).

This Series was described from the Lower Hunter District and named by T. W. E. David and Sussmilch (1919), and was assumed to succeed the Lower Carboniferous Burindi Series. This region thus became known as the type-area, and later was intensively studied by Osborne (1922-1925), but subsequent researches in other districts by W. R. Browne and S. W. Carey (see 1938, p. 591) established the contemporaneity of the Lower Kuttung Series (the Basal and Volcanic Stages of Osborne) and the Upper Burindi, both of these stratigraphical units being approximately synchronous with the Viséan of Europe.

In all places in N.S.W. where the terrestrial Kuttung Series has been studied a lower dominantly volcanic section and an upper dominantly glacial section have been recognised, although evidences of vulcanism over a wide area during the Glacial Stage are forthcoming in the development of the Paterson type of toscanite-dellenite lavas, and many pyroclastic units interbedded with glacial sediments. Nevertheless, the period of the Lower Kuttung witnessed an intensive vulcanicity probably greater than that of any other Palæozoic epoch. This was succeeded, after a lapse of time and some diastrophic activity, by relatively quiet conditions with extensive clastic sedimentation in the Lower Glacial Stage of the Upper Kuttung. The Upper Glacial Stage was marked by local volcanic activity in a number of places, as at Stroud, Raymond Terrace District, Pokolbin and Stanhope, but elsewhere was characterised by accumulation of glacial sediments, with an absence of lava and true pyroclastic deposits.

In earlier papers upon the Lower Hunter and Karuah Districts, the writer dealt in detail with the stratigraphy and petrography, but refrained from

discussing critically the broader aspects and petrogenetic significance of the lava-sequences, and the mode of development and/or accumulation of the pyroclastic rocks. This policy was followed because of the imperfect state of our knowledge of the problems involved.

The present paper deals mainly with the great volcanic succession of the Lower Kuttung, although the Upper Kuttung will be considered to some extent.

The aims of the paper may be stated to be as follows :

- (a) To review the salient facts about the volcanicity in the light of information from researches upon the *nuée ardente* type of eruption.
- (b) To describe the field occurrence and widespread distribution of the ignimbrites in the succession.
- (c) To relate the time of the ignimbrite-development to the general framework sequence of the Volcanic Stage.
- (d) To discuss the mode of origin of the deposits.

Some chemical analyses of the Kuttung lavas will be cited, and petrographic details sufficient to justify the determination of some of the rocks as *ignimbrites* will be given. However, full chemical study and critical textural and mineralogical investigations will be necessary before one can appreciate fully the remarkable volcanicity of Carboniferous times in N.S.W.

FRAMEWORK SEQUENCE OF THE LOWER KUTTUNG.

(a) *The Lower Hunter Region.*

In 1919 (p. 288) W. R. Browne pointed out the general character of the Kuttung lava sequence, drawing attention to the main feature of a general decreasing basicity, with concentration of andesites at the base of the Volcanic Stage, of dacitic and toscanitic rocks in the central portion, and of rhyolitic types in the upper part. He gave a succinct account of the mineralogical and textural relationships of the lavas, as then known.

In 1925 the writer stated the following as the framework sequence for the Clarendon-Paterson District (No. 1 being the oldest unit) :

7. Dacites.
6. Potash Rhyolites.
5. Toscanite-Dellenite Group (Mt. Gilmore Type).
4. Dacites.
3. Quartz Keratophyres (Williams River Type).
2. Pyroxene Andesites (Hudson's Peak Type).
1. Hornblende Andesites (Martin's Creek Type).

As pointed out by various workers, there are many places where the framework sequence is much extended or "filled-out", as it were, by an abundance of lavas and tuffs which are peculiar to the respective localities of occurrence, and which sometimes present unusual features.

This is particularly the case with the Eelah-Gosforth District (Browne, 1926) and the Stanhope District (Scott, 1947). In the former there are acid rocks below the andesites of the Volcanic Stage, and there is a repetition of hornblende and pyroxene andesite units. In the Stanhope District a remarkable development of intermediate and acid rocks underlies those lavas which throughout the Lower Hunter, are regarded as marking the beginning of eruptions in the Volcanic Stage.

Correlations of the Sequences in the Lower Hunter Areas.

Not much has been published regarding the correlation of outstanding lavas and tuff horizons in the Lower Kuttung Series, although various workers

have had the subject much in mind, and considerable discussion has been engaged in, so that some ideas have become fixed regarding the equivalence of certain indicator horizons in separated localities.

Sussmilch (1923) set up certain correlations of sections in the Volcanic Stage but made some deductions which have proved erroneous. Browne (1926) explained certain broad correlations between the Gosforth District and the type areas further east. Miss Scott (1947) attempted to effect some detailed correlations between the Stanhope-Gosforth area and the type-area, and illustrated her views with columnar sections. In regard to these the author would venture the opinion that not all the suggested correlations are correct. First, though the basal andesites of the Volcanic Stage in the Seaham-Clarencetown area are correctly linked with similar flows at Gosforth and Stanhope, the higher andesites found in the latter places have no counterparts in the type-area. Secondly, in spite of his original statement (Osborne, 1922, 167) the author is not now satisfied that the Basal Stage as exposed in the type-area is present at Gosforth and Stanhope, since the sequence so designated there by Miss Scott has hitherto yielded no traces of the characteristic flora. It includes a number of lava-flows, and is perhaps better regarded as a downward extension of the Volcanic Stage.

The following correlations are given here as a result of mature consideration of the Kuttung succession across the whole of the Lower Hunter-Karuah region

(1) *The Martin's Creek Andesite Horizons (lithoidal and glassy)* may be traced from the Girvan District, on the east, through the Volcanic Stage belt which runs along the western side of the Stroud-Gloucester Trough. The andesite outcrops on the roadside about six miles east of Dungog and continues southwards to Clarencetown. (Beyond this point the regional distribution in the type area has already been published.) It can then be traced northward from Paterson towards Gresford, and suffers much faulting between this locality and Gosforth-Stanhope. The strict correlation in the latter area equates the horizons on the lower slopes of Hudson's Peak with those of Martin's Creek. These horizons of Hb. Andesite do not occur to the west or north of the Cranky Corner-Glendonbrook district. The intervention of the Webber's Creek fault and the Hunter Thrust have cut out possible extensions.

(2) *The Hudson's Peak type of pyroxene andesite and pitchstone* can be traced almost as satisfactorily as the amphibole types. The areas of greatest development are at Hudson's Peak, Stanhope and Balikera, near Seaham. West of the Stanhope area there are several flows of this type in the areas near the Hunter Thrust Line and elsewhere. In almost every case the associated strata indicate the validity of correlating them with the lower units found on Hudson's Peak.

(3) *The Williams River Quartz Keratophyre* is an intensely albitised dacite or toscanite, according to the area chosen. It does not occur in the Karuah Valley but can be traced from Limeburner's Creek through the complexly-faulted areas westward to Vacy and Gresford, eventually to appear at Eelah, Gosforth and Stanhope, being the first important flow to succeed the upper Hb. Andesites of those districts. Beyond this locality this horizon is absent from the sequence.

(4) *The Mt. Gilmore Toscanite-Dellenite Group*, over a wide area, has been proved a most reliable stratigraphical index.

This horizon varies through a limited range of composition, and also varies somewhat in texture, but is mostly medium to coarse-grained in its phenocrystic content.

A great development of this unit is seen around the nose of the Girvan anticline, east of Booral, and especially also along its western side. Thus the

rugged hills flanking the Lower Karuah River on the east side are made of thick flows of this rock. The dominant ridges of toscanite on either side of the Stroud-Gloucester Trough are directly to be correlated with the Mt. Gilmore horizon.

Beyond the type area, the toscanite is found strongly developed at Eelah Gap and along the Rosebrook Ridge westward to Stanhope. West of Glendonbrook it peters out and is unknown from the great areas of Volcanic Stage rocks in the middle Hunter Valley.

With few exceptions we cannot confidently correlate the many horizons of dacite, soda rhyolite, potash rhyolite and sodi-potassic types across areas of significant dimensions. Some very local linkings can be made, of course. The main point to emphasise, however, is that acid and sub-acid rocks are characteristic, as a group, of the top of the Volcanic Stage.

(b) *The Middle Hunter Region.*

The Kuttung Belt which outcrops along the north-eastern side of the Middle Hunter Valley displays a sequence in the Volcanic Stage which is distinctly different from that of the areas dealt with above.

The important Kuttung areas in the Middle Hunter region are the Mirrannie-Dyrring, Glennie's Creek-Muswellbrook and the Mid-Rouchel-Bowman's Creek districts.

The framework sequence is incomplete because of the truncating effect of the Hunter Thrust all along the bounding zone between Glendonbrook and Muswellbrook.

The chief features of the sequence are :

- (a) The presence of the pyroxene andesite in the lower stratigraphical zones.
- (b) The abundance of *ignimbrites*, viz. on four main horizons, previously described as the Bridgman, Sedgfield, Westbrook and Glendonbrook Felsites (Osborne, 1926).
- (c) The concentrated incidence of dacites a little above the topmost *ignimbrite*.
- (d) The remarkably constant development of flows of typical Hb. Andesite at the top of the Volcanic Stage.

The skeleton sequence, therefore, is as follows, proceeding from older to newer : pyroxene andesites, ignimbrites, dacites and hornblende andesitic pitchstones. Various local modifications occur in this province, the chief examples being (a) the development of a group of spherulitic lavas in the Cross Creek area, north-west of Singleton, and (b) the appearance of an extra group of hornblende andesites in the Muscle Creek Section.

LOWER KUTTUNG TUFFS, FLOW-BRECCIAS AND RELATED TYPES.

Throughout the Lower Kuttung there is a great development of true pyroclastic rocks and of tuffaceous deposits which are due to admixture of ash and sedimentary units accumulated mainly sub-aqueously, but occasionally in a piedmont environment. The more strictly igneous of the tuffaceous groups are medium to fine-grained, and show wide variation of composition, with a preponderance of biotite-dacite tuff in the lowermost zones and a predominance of soda-rhyolite tuff in the upper levels of the succession.

The totally pyroclastic rocks comprise (a) autobrecciated rhyolites, dacites and felsites, and (b) agglomerate and breccia formed by the accumulation of falling fragments from paroxysmal eruptions of fairly restricted extent.

Since recording in earlier papers the occurrence and petrography of many of these clastic rocks, the writer has been assembling data concerning their relationships with the facts of sequence and composition of the flows in the various neighbourhoods.

It can now be assumed that specialised centres of eruption have been responsible for great variety and overlapping of small flows in areas where flow-breccias and shatter-agglomerates are developed.

Following this line of enquiry it now becomes possible to postulate centres of eruption having considerable influence in overlapping, yet not controlling the distribution of the leading flows of the framework sequence.

Thus, partly based on the evidence of the tuff and breccia occurrences, we recognise the following centres in the Lower Kuttung :

- (a) Muscle Creek, east of Muswellbrook.
- (b) Cross Creek, north of Singleton.
- (c) Bridgman District.
- (d) Mirannie Area.
- (e) Breckin Area.
- (f) Gosforth District.
- (g) Stanhope District.
- (h) Pokolbin District.
- (i) Martin's Creek District.
- (j) Glenoak District.
- (k) Mt. Gilmore, near Clarencetown.
- (l) Booral and East Stroud.
- (m) North Stroud-Weistmantels.

All through the present discussion it has been assumed that the framework sequence which holds so well over widespread localities, covering as much as 3,000 square miles, is the expression of a regional magmatic differentiation, and a regional control in serial eruptions, based upon widespread fissuring throughout large tracts whose geotectonic condition was related to a tensional environment, dependent upon gravity or isostatic controls.

VULCANICITY OF THE UPPER KUTTUNG SERIES.

The chief features of the volcanic succession in the Upper Kuttung Series in the region under notice are :

- (i) The widely developed toscanite-dellenite lavas of the Paterson Type, which occupy a constant stratigraphical position.
- (ii) The specialised occurrence of varied lava sequences in the upper part of the Glacial Stage.

It is clear that the Paterson lavas and associated pumiceous tuffs indicate the widespread revival of volcanic activity marked by fissure eruptions of a toscanite almost identical with an earlier fissure product (the Mt. Gilmore Toscanite). The Paterson Type has been studied from the whole of the Kuttung Belt lying between Raymond Terrace and the Mirrannie-Bowman's Creek region. Beyond this the flows die out and are absent from the Upper Hunter Kuttung areas. The rocks grade from toscanite to dellenite, but as a group are markedly constant, petrologically.

High up in the Glacial Stage at Pokolbin, and also at Stanhope and Stroud, there is a noteworthy development of lavas embracing alkaline types such as trachyte and trachy-basalt, also flows of basalt. Small amounts of basalt have been recorded from elsewhere, but in the Stroud-Weistmantels sector there is a strong development of the basic rock.

It is clear that towards the end of Kuttung time there was developed, in response to local stress conditions, a series of strongly differentiated centres of

magmatic activity, by which the usual calcic series of andesite-dacite-rhyolite was modified by the incoming of alkaline types. At the same time basalts with alkaline affinities began to appear. Until considerable chemical and petrological information regarding these basalts is forthcoming it would be inadvisable to endeavour to relate them to the Kuttung sequences.

The presence of ignimbrites in the Glacial Stage at Stroud is a feature of Kuttung vulcanicity hereabouts. Two horizons are well represented (see section below). The outcrops of the upper ignimbrite to the west of the Pacific Highway about $1\frac{1}{2}$ miles south of Stroud Road recall vividly the field appearance of the well-known New Zealand type, Wilsonite, described by Marshall.

CHEMICAL ANALYSES

Below is given a list of analyses of representative lava-members of the Kuttung Succession. It is to be regretted that no unit which can be confidently interpreted as an ignimbrite has been analysed. No worth-while petrogenic discussion of the Kuttung lavas is yet possible, because so many of the rocks have been profoundly altered by deuteric processes, especially that of *albitisation*. Until a much greater amount of chemical data is available, one deprecates any attempt to discuss, more or less comprehensively, the chemical problems of the Kuttung vulcanicity.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. |
|-----------------------------------|--------|--------|--------|-------|--------|--------|--------|--------|--------|
| SiO ₂ .. | 64.20 | 64.88 | 61.10 | 67.06 | 73.04 | 73.90 | 72.98 | 77.82 | 75.06 |
| Al ₂ O ₃ .. | 16.88 | 16.18 | 16.20 | 15.95 | 13.86 | 11.95 | 12.58 | 11.46 | 14.21 |
| Fe ₂ O ₃ .. | 1.90 | 1.52 | 2.00 | 1.78 | 1.60 | 1.70 | 0.28 | 0.30 | 1.31 |
| FeO .. | 2.52 | 2.43 | 3.78 | 2.37 | 0.45 | 0.99 | 1.66 | 0.09 | 0.27 |
| MgO .. | 0.66 | 1.21 | 3.55 | 1.87 | 0.48 | 0.55 | 0.49 | 0.23 | 0.09 |
| CaO .. | 3.14 | 3.00 | 4.90 | 1.98 | 1.44 | 1.50 | 2.81 | 0.22 | 0.42 |
| Na ₂ O .. | 4.41 | 5.41 | 3.42 | 4.62 | 3.40 | 3.10 | 4.80 | 0.86 | 6.88 |
| K ₂ O .. | 3.52 | 2.79 | 2.83 | 2.01 | 4.39 | 4.74 | 2.99 | 7.19 | 0.58 |
| H ₂ O+ | 1.79 | 1.63 | 1.03 | 0.65 | 0.79 | 1.37 | 0.79 | 1.40 | 0.62 |
| H ₂ O— | 0.31 | 0.50 | 0.53 | 0.44 | 0.25 | 0.21 | 0.43 | 0.36 | 0.56 |
| CO ₂ .. | 0.03 | tr. | abs. | abs. | abs. | abs. | abs. | 0.03 | — |
| TiO ₂ .. | 0.65 | 0.89 | 0.55 | 0.40 | 0.22 | 0.20 | 0.40 | 0.02 | abs. |
| P ₂ O ₅ .. | 0.13 | tr. | 0.21 | 0.28 | 0.04 | 0.05 | 0.08 | 0.04 | 0.03 |
| MnO .. | — | 0.05 | tr. | 0.39 | 0.07 | 0.06 | 0.03 | tr. | 0.04 |
| BaO .. | — | — | tr. | — | 0.04 | 0.06 | — | 0.02 | — |
| etc. | | | | | | | | | |
| | 100.14 | 100.49 | 100.10 | 99.80 | 100.07 | 100.38 | 100.32 | 100.04 | 100.07 |

I. Hb. Andesite, Martin's Creek. Anal. G. D. Osborne.

II. Hb. Andesite, Martin's Creek. Anal. W. G. Stone.

III. Pyroxene Andesite (Hudson's Peak Type), Pokolbin. Anal. W. A. Greig.

IV. Qtz. Keratophyre (Williams River Type), Clarencetown. Anal. G. D. Osborne.

V. Toscanite, Mt. Gilmore. Anal. W. A. Greig.

VI. Toscanite (Mt. Gilmore Type), Port Stephens. Anal. W. G. Stone.

VII. Toscanite, Paterson. Anal. G. D. Osborne.

VIII. Rhyolite, Mt. Bright, Pokolbin. Anal. J. C. H. Mingaye.

IX. Soda Rhyolite, Paddy's Hill, north of Raymond Terrace. Anal. W. A. Greig.

THE IGNIMBRITES.

Previous Recognition of Ignimbrites in the Kuttung Succession.

In 1923 the writer visited New Zealand and studied the occurrence and petrography of the ignimbrites of the North Island, after the advantage of full discussion of these rocks with Dr. P. Marshall, who first interpreted the rhyolitic

rocks of the Great Volcanic Plateau as compacted material ejected as *nuées ardentes* (Marshall, 1932). Subsequently, in 1934, in an address to the Geological Section of the Royal Society of N.S.W. upon the N.Z. ignimbrites (see *THIS JOURNAL*, Vol. 68, p. xlviii), specimens of certain Kuttung rocks were exhibited and the opinion expressed that these were ignimbrites.

Quite recently Beryl Scott (1947) has recorded the presence of ignimbrites in the Volcanic Stage in the Stanhope District, and has given somewhat meagre metrographic accounts of these.

Since suggesting an ignimbritic origin for many of the volcanic units hitherto described from the Kuttung as rhyolites, and rhyolitic tuffs, the writer has been assembling evidence of the widespread occurrence of these fascinating rocks in the Hunter and Karuah River Districts.

(It is pertinent to mention here that in 1934 H. C. Richards and W. H. Bryan discussed the mode of origin of part of the Brisbane Tuff and concluded that it paralleled very closely the ignimbrites of New Zealand.)

Field Occurrence.

The ignimbrites of the N.S.W. Carboniferous are distinctive in their field relations, occurring in relatively thin units which are remarkably persistent over large areas. The thickness varies up to a maximum of 120 feet, but generally is small and of the order of 12–20 feet. The rocks are light coloured with marked “fluidal” texture, and show in many areas a rude prismatic jointing more or less perpendicular to the “flow structure”. This jointing does not pass into the associated rocks, nor is it related genetically to any tectonic features of the surrounding country. It is essentially syngenetic, and this recalls the prevalence of syngenetic jointing in the New Zealand ignimbrites. Marshall interprets this as evidence against a rock with flow structure consolidating from a molten condition. (It is interesting to note that in several early papers published by the writer before the concept of ignimbrites was forthcoming, reference to this jointing was made, although its significance was not known.)

It always has been difficult to explain the “flow” structures and the extremely extended outcrops of the ignimbrites, if they were to be regarded as acid flows. With high viscosity characteristic of the rock-types under consideration, considerable flowing of the magma would have been unlikely, and the regularity of the flow-layers would almost certainly have been obliterated or modified by flow-breccia structures.

In two or three places in the Middle Hunter area it is possible to see evidence that the ignimbrite was developed on a very uneven floor, and reconstruction of the physiography of the localities in question indicates that the igneous rock (if a flow) travelled “uphill” considerably. With more and more field work in recent years, it has become necessary to invoke some special mode of development different from accepted ideas of the ordinary flow of lava, to explain the units now being discussed. Accordingly I have concluded that the rocks in question have had essentially the same mode of origin as the ignimbrites described by Marshall. Some fuller explanation of this view is given below.

Petrography.

The ignimbrites vary in grainsize, and may be very heterogeneous on a small scale, while at other times exhibiting an even-textured “ground” through which are strung axiolites, beaded concentrations of spherulites, and comb-like structures in fibrous feldspathic and siliceous material. Many shards and tubes of pumice and myriad cusped fragments and shreds of glassy material are packed into a solid mass with pseudo-fluidal texture, giving distinctive fracture and variable lustre from surface to surface.

LOWER KUTTUNG IGNIMBRITE HORIZONS

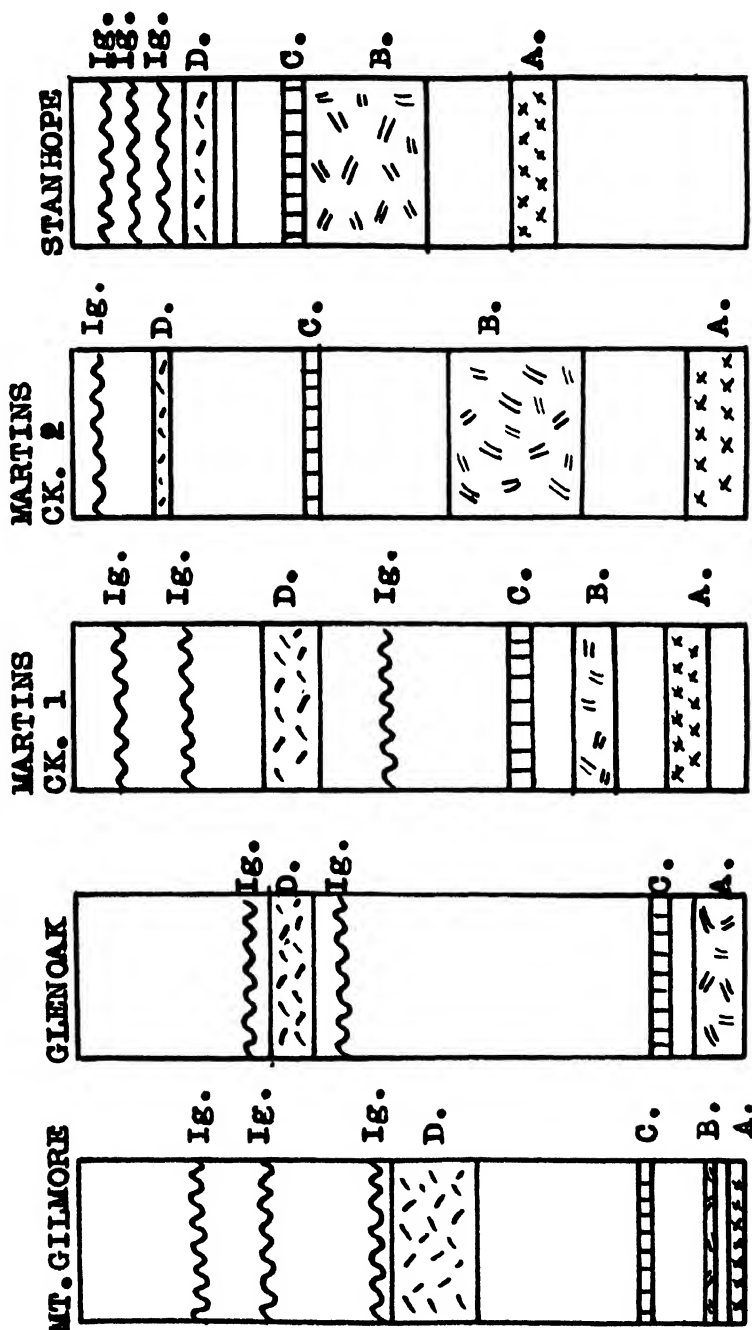


Fig. 1.—A. signifies Martin's Creek horizon. B. Hudson's Peak horizon. C. Williams River horizon. D. Mt. Gilmore horizon. Ig. Ignimbrite. Thickness of sections given in text. (Note.—In the Glenoak Section the lowest unit should be marked B, not A.)

There is a suggestion of dense silicification or of devitrification in many rocks. While patches are glassy, the bulk of the rocks are now lithoidal or felsitic.

The rocks show no scoriaceous or ropy texture at the upper surface, although the apparent flow structure is so marked in the body of the rock. Uniformity of colour (mostly pink or cream) is a feature over wide areas and there is an absence of abrupt passage from fluidal rock into brecciated material, such as is seen with many of the normal Kuttung flows. No autoclastic structure or twisted flow-fabric occurs in the ignimbrites, such as is seen in modern lavas whose origin is not in doubt.

Microscopically, the ignimbrites are very difficult of satisfactory study, and it is not proposed to discuss the petrography in full, as this will be taken along with a chemical study of these rocks in the future. It is sufficient to note that the "phenocrystic" minerals commonly developed are quartz, oligoclase or albite, biotite, and a variable amount of orthoclase. Rarely altered hornblende is seen, and occasionally one or two pieces of what appear to be hypersthene. These units (of approximately uniform grainsize up to a maximum of 2 mm.) are set in a devitrified pumiceous groundmass of fine silica and feldspathic material, through which are threaded abundant axiolitic and genetically kindred structures.

Many of the tubular or shred-like fragments bend around the "phenocrysts" of albite and quartz and indicate clearly a plastic condition prior to crystallisation.

Stratigraphical Horizons.

Text-figure 1 indicates the stratigraphical relationships of the ignimbrite deposits, the chronological positions of the postulated eruptions being summarised thus :

- (a) There is a pronounced concentration towards the upper part of the Volcanic Stage, the Stanhope Section being the only one in which an ignimbrite has been recorded from low down in the sequence.
- (b) Within the Volcanic Stage most of the ignimbrites are above the horizon of the Mt. Gilmore toscanite although in two sections an ignimbrite zone marks the infra-toscanite series.
- (c) In the Glacial Stage there are two ignimbrite horizons, these being respectively below and above the horizon of the Paterson toscanite.

It would thus appear that the special eruptive conditions for the production of ignimbrites obtained at several distinct times in the areas now being considered. These violent conditions occurred in the Upper Volcanic Stage and the Mid-to-Upper Glacial Stage.

DETAILED STRATIGRAPHICAL SECTIONS SHOWING IGNIMBRITE HORIZONS.

It is proposed in this section to restate certain sections of the Volcanic Stage, already published, and to record a new section from the Glacial Stage, for the purpose of placing on record the stratigraphical positions, and the stratigraphical concentration of ignimbrites in the Kuttung succession. (All sections descend stratigraphically.)

- (a) *The Mt. Gilmore Section* (Osborne, 1922, p. 172).

| | Feet |
|---------------------------------|------|
| Tuffs | 45 |
| Volcanic conglomerate | 50 |
| Tuffs with pebbly bands | 130 |
| Potash rhyolite | 50 |
| <i>Ignimbrite</i> | 50 |
| Conglomerate | 80 |
| Potash rhyolite | 40 |
| Conglomerates | 90 |

| | |
|--|-------|
| Keratophyre | 90 |
| Conglomerate | 50 |
| <i>Ignimbrite</i> | 100 |
| Red potash rhyolite | 60 |
| Conglomerate | 150 |
| <i>Ignimbrite</i> | 70 |
| Tuffaceous conglomerate | 45 |
| <i>Ignimbrite</i> | 60 |
| Tuffs with felsite | 80 |
| Dellenite-Toscanite (Mt. Gilmore Type) | 400 |
| Conglomerate | 320 |
| Rhyo-dacite | 150 |
| Bi. Qtz. keratophyre (Williams River type) | 105 |
| Conglomerate | 30 |
| Bi. Qtz. keratophyre (Williams River type) | 150 |
| Conglomerate | 75 |
| Sodi-potassic rhyolite | 45 |
| Conglomerate | 80 |
| Pyroxene andesite (Hudson's Peak type) | 50 |
| Pebbly tuff | 150 |
| Hornblende andesite (Martin's Creek type) | 80 |
| Total | 2,875 |

(b) *The Glenoak Section* (Osborne, 1922, p. 175).

| | |
|--|-------|
| | Feet |
| Dacite | 120 |
| Sodi-potassic rhyolite | 45 |
| <i>Ignimbrite</i> | 130 |
| Rhyolite | 250 |
| Dellenite (Mt. Gilmore type) | 80 |
| Conglomerate | 45 |
| <i>Ignimbrite</i> | 40 |
| Fine-grained quartz keratophyre | 90 |
| Conglomerate | 450 |
| Felsite | 60 |
| Conglomerate | 180 |
| Fine tuff | 60 |
| Coarse tuff | 100 |
| Volcanic conglomerate, etc. | 60 |
| Bi. Qtz. keratophyre (Williams River type) | 180 |
| Pebbly tuff | 100 |
| Pyroxene andesite glass (Hudson's Peak type) | 200 |
| Total | 2,190 |

(c) *Martin's Creek, Section No. 1* (Osborne, 1922, p. 177).

| | |
|---|-------|
| | Feet |
| Tuffs | 200 |
| <i>Ignimbrite</i> | 30 |
| Dacite | 100 |
| Flow-breccias | 80 |
| <i>Ignimbrite</i> | 25 |
| Pebbly tuff | 185 |
| Toscanite (Mt. Gilmore type) | 210 |
| Tuffaceous conglomerate | 200 |
| <i>Ignimbrite</i> | 80 |
| Tuff | 70 |
| Conglomerate | 65 |
| Bi-Qtz. keratophyre (Williams River type) | 85 |
| Conglomerate | 100 |
| Pyroxene andesite (Hudson's Peak type) | 80 |
| Pebbly tuff | 100 |
| Hornblende andesite (Martin's Creek type) | 200 |
| Total | 1,810 |

(d) *Martin's Creek, Section No. 2* (Osborne, 1922, p. 178).

| | Feet |
|---|------|
| <i>Ignimbrite</i> | 50 |
| Cherty tuff | 25 |
| Fine-grained tuffs | 15 |
| Volcanic conglomerate | 10 |
| Conglomerate | 15 |
| Toscanite (Mt. Gilmore type) | 50 |
| Soda-felsite | 100 |
| Red potash-rhyolite | 25 |
| Coarse conglomerate | 300 |
| Bi-Qtz. keratophyre (Williams River type) | 50 |
| Total | 640 |

(e) *The Stanhope Section* (Scott, 1947).

| | Feet |
|--|-------|
| Dacite tuffs with several <i>Ignimbrite</i> horizons (relatively thin) | 800 |
| Toscanite (Mt. Gilmore type) | 260 |
| Conglomerate | 180 |
| Toscanite (on horizon of Williams River keratophyre) | 400 |
| Hornblende andesite | 900 |
| Pyroxene andesite (Hudson's Peak type) | 1,200 |
| Conglomerate | 350 |
| Hornblende andesite (Martin's Creek type) | 130 |
| Conglomerate | 160 |
| <i>Ignimbrite</i> | 30 |
| Conglomerate | 250 |
| Felsite | 130 |
| Fluvio-glacial conglomerate | 450 |
| Pyroxene andesite | 50 |
| Conglomerate | 50 |
| Rhyolite | 920 |
| Pyroxene andesite | 660 |
| Conglomerate | 100 |
| Rhyolite | ? |
| Total, at least | 7,020 |

(f) *The Bridgman Section* (Osborne, 1926, p. 391).

| | Feet |
|---|-------|
| Hornblende andesite | 200 |
| Conglomerate and tuff | 150 |
| Hornblende andesite | 50 |
| Conglomerate | 170 |
| Hæmatitic flow-breccia | 20 |
| <i>Ignimbrite</i> | 30 |
| Felsite | 15 |
| <i>Ignimbrite</i> | 20 |
| Conglomerate with hæmatitic lava band | 250 |
| <i>Ignimbrite</i> | 30 |
| Conglomerate | 220 |
| <i>Ignimbrite</i> | 30 |
| Conglomerate and tuffs | 150 |
| <i>Ignimbrite</i> | 40 |
| Conglomerate and tuff | 60 |
| Total | 1,435 |

(g) *The Muscle Creek Section* (Osborne, 1928, p. 568).

| | Feet |
|---------------------------------|------|
| Tuffaceous conglomerate | 300 |
| Felsite | 80 |
| Tuffaceous conglomerate | 200 |
| Dacite | 100 |
| Coarse conglomerate | 400 |
| Biotite felsite | 50 |

| | | | | | | | | |
|------------------------|----|----|----|----|----|----|----|-------|
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | 300 |
| Hb. andesite glass | .. | .. | .. | .. | .. | .. | .. | 80 |
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | 200 |
| Fine tuff | .. | .. | .. | .. | .. | .. | .. | 300 |
| Coarse tuff | .. | .. | .. | .. | .. | .. | .. | 100 |
| Acid tuff | .. | .. | .. | .. | .. | .. | .. | 170 |
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | 100 |
| Andesitic conglomerate | .. | .. | .. | .. | .. | .. | .. | 90 |
| Soda felsite | .. | .. | .. | .. | .. | .. | .. | 60 |
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | 200 |
| Tuff | .. | .. | .. | .. | .. | .. | .. | 80 |
| Dacites (devitrified) | .. | .. | .. | .. | .. | .. | .. | 245 |
| Tuff | .. | .. | .. | .. | .. | .. | .. | 100 |
| Ignimbrite | .. | .. | .. | .. | .. | .. | .. | 120 |
| Coarse tuff | .. | .. | .. | .. | .. | .. | .. | 300 |
| Ignimbrite | .. | .. | .. | .. | .. | .. | .. | 150 |
| Tuff and conglomerate | .. | .. | .. | .. | .. | .. | .. | 200 |
| Dacite | .. | .. | .. | .. | .. | .. | .. | 170 |
| Tuff and conglomerate | .. | .. | .. | .. | .. | .. | .. | 95 |
| Ignimbrite | .. | .. | .. | .. | .. | .. | .. | 85 |
| Tuff | .. | .. | .. | .. | .. | .. | .. | 200 |
| Soda felsite | .. | .. | .. | .. | .. | .. | .. | 90 |
| Tuff and conglomerate | .. | .. | .. | .. | .. | .. | .. | 230 |
| Total | .. | .. | .. | .. | .. | .. | .. | 4,795 |

(h) The Stroud Section (Generalized).

| | | | | | | | | | |
|-------------------------|----|----|----|----|----|----|----|----|-------|
| | | | | | | | | | Feet |
| Basalt | .. | .. | .. | .. | .. | .. | .. | .. | 200 |
| Andesitic tuff | .. | .. | .. | .. | .. | .. | .. | .. | 150 |
| Ignimbrite | .. | .. | .. | .. | .. | .. | .. | .. | 25 |
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | .. | 20 |
| Hb. andesite | .. | .. | .. | .. | .. | .. | .. | .. | 20 |
| Rhyolite | .. | .. | .. | .. | .. | .. | .. | .. | 25 |
| Dacite | .. | .. | .. | .. | .. | .. | .. | .. | 50 |
| Coarse conglomerate | .. | .. | .. | .. | .. | .. | .. | .. | 30 |
| Tuffs with pebbles | .. | .. | .. | .. | .. | .. | .. | .. | 560 |
| Basalt | .. | .. | .. | .. | .. | .. | .. | .. | 150 |
| <i>Rhacopteris</i> tuff | .. | .. | .. | .. | .. | .. | .. | .. | 20 |
| Conglomerate | .. | .. | .. | .. | .. | .. | .. | .. | 100 |
| Ignimbrite | .. | .. | .. | .. | .. | .. | .. | .. | 15 |
| Sandy tuffs | .. | .. | .. | .. | .. | .. | .. | .. | 120 |
| Total | .. | .. | .. | .. | .. | .. | .. | .. | 1,485 |

MODE OF ORIGIN OF THE IGNIMBRITES.

It is the opinion of the writer that the ignimbrites here discussed have been formed after the manner described by Marshall for the N.Z. occurrences. That is to say they are due to the welding together of tuffaceous material given out in the incandescent state from fissures, and carried with swift velocity to places of accumulation. Thus they are the products of a series of *nuées ardentes*.

It is considered that the eruptions were of the *Katmaian Type*, in the nomenclature of Lacroix. This type, as opposed to the *Pelean* eruption (which takes place in a restricted crater) involves the supply of material from fissures. It is essential, in considering the origin of these fascinating rocks, that we should draw from the experience that scientists have had in observing modern eruptions of the "glowing cloud" or *nuée ardente* type. Fortunately the literature upon this subject is already considerable, and reputable geologists and petrologists have described phenomena observed by them, or have carefully investigated the recent products of outbursts of this kind. (See Flett, 1908; Jagger, 1903; Perrett, 1935; Lacroix, 1904; Macgregor, 1936, 1938; and Marshall, 1932, 1935). Thus we may postulate that shreds and chips of glassy material have

been produced by a frothing over and instantaneous shattering of pumiceous lava very rich in gas. Fairly large volumes of finely divided material have been involved in the accumulation of some of the thicker ignimbrites.

It is probable that in the areas of the Lower and Middle Hunter in Kuttung times there were alternations of eruptive controls, so that three types of vulcanicity affected the region from time to time. These were responsible at different epochs for

- (a) welling out of lava flows from fissures ;
- (b) explosive discharge of ash, pumice, tuffs, boulders, lapilli, etc., all at a temperature such that on falling to the ground no further vulcanological processes would be likely to continue ;
- (c) intensively gaseous and explosive eruptions of the *nuée ardente* type.

Apparently some of the products due to the second type of control would be pure tuffs or breccias while others would be contaminated by sediment. Very local eruptions would produce agglomerate and breccia-filled necks. In cases of eruptions of type (a), two cases would arise. Either homogeneous lava not greatly charged with volatiles would spread uniform flows over wide areas, or inhomogeneous lava would give rise to streaky and layered extrusions. Both products are encountered in the Kuttung fields, but the former is, of course, the prevalent type. An example of the latter is that of the heterogeneous felsite at the foot of the Hudson's Peak Section, near Gosforth.

Prevalence of Gas in Ignimbrite Eruptions.

Vulcanologists who have studied the origin and mode of accumulation of *nuées ardentes* emphasise that an important determining factor in the sudden development of an incandescent cloud from partly consolidated rock material and volcanic gases is the course of the gas-history in the time just prior to the climax of eruption. If gas is prevented from escaping from the vent, the lava is unrelieved by effervescence and the condition is reached when expansion produces a frothing pumice due to violent action breaking through any residual crust. Thus is caused the ejection of incandescent material. Reactions between liberated gases help to keep glowing the various fragments (large and small). Solidification of glassy blebs will set free gas, thus producing porous texture in some of the solid ingredients of a *nuée ardente*.

It is clear that the various grades of material which have frothed over will settle down in some sort of density-controlled stratification, even though the accumulation has been rapid and of avalanche character.

Rocks similar to the ignimbrites of New Zealand have been formed by recent or modern eruptions in the West Indies, Katmai Province of Alaska, Yellowstone National Park, Crater Lake (Oregon) and elsewhere (see Bibliography).

SUMMARY.

An account is given of the salient features of the Kuttung Vulcanicity in the Hunter-Karuah District, particular attention being given to the occurrence of welded pumiceous tuffs, known in New Zealand as *ignimbrites*. The stratigraphical incidence of the *ignimbrite* horizons is made clear by the statement of many detailed sections from the area. These fascinating units in the volcanic succession are shown by their features of (a) texture, (b) field occurrence, and (c) vulcanological environment, to correspond almost exactly to products of the Katmaian type of the *nuée ardente* type of eruption.

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IDA A. BROWNE, D.Sc.
Honorary Editorial Secretary

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE
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Particulars regarding the preparation of manuscripts of papers for publication in the Society's Journal are to be found in the "Guide to Authors", which is obtainable on application to the Honorary Secretaries of the Society.

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P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

† Life Members.

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| | | |
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| 1944 | | Adamson, Colin Lachlan, Chemist, 36 McLaren-street, North Sydney. |
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| 1935 | | †Albert, Michael Francois, "Boomerang," Billyard-avenue, Elizabeth Bay. |
| 1898 | | †Alexander, Frank Lee, Surveyor, 5 Bennett-street, Neutral Bay. |
| 1941 | | †Alldis, Victor le Roy, I.S., Registered Surveyor, Box 57, Orange, N.S.W. |
| 1948 | | Anderson, Geoffrey William, B.Sc., 37 Elizabeth-street, Allawah. |
| 1948 | P 2 | Andrews, Paul Burke, Department of Geology, University of Sydney; p.r. 5 Conway-avenue, Rose Bay. |
| 1930 | P 1 | Aston, Ronald Leslie, B.Sc., B.E. <i>Syd.</i> , M.Sc., Ph.D. <i>Camb.</i> , A.M.I.E. <i>Aust.</i> , Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield. (President, 1948.) |
| 1919 | P 1 | Arousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah. |
| 1935 | | Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown. |
| 1949 | P 2 | Backhouse, James Roy, M.Sc. <i>Syd.</i> , Lecturer, Sydney Technical College; p.r. Fowler-avenue, Bexley North. |
| 1924 | P 2 | Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Professor of Experimental Physics in the University of Sydney. |
| 1934 | P 2 | Baker, Stanley Charles, M.Sc., A.Inst.P., Head Teacher of Physics, Newcastle Technical College, Tighe's Hill; p.r. 8 Hewison-street, Tighe's Hill, N.S.W. |
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| 1949 | | Ball, Reginald Arthur, Industrial Chemist, 25 George-street, Sydney. |
| 1946 | P 1 | Barclay, Gordon Alfred, Chemistry Department, Sydney Technical College, Harris Street, Ultimo, N.S.W.; p.r. 78 Alt Street, Ashfield. |
| 1919 | | Bardsley, John Ralph, 76 Wright's-road, Drummoyne. |
| 1947 | | Beckmann, Peter, A.S.T.C., Lecturer in Chemistry, Technical College, Wollongong. |
| 1933 | | Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff. |
| 1926 | | Bentivoglio, Sydney Ernest, B.Sc.Agr., 42 Telegraph-road, Pymble. |
| 1940 | | Betty, Robert Cecil, 67 Imperial-avenue, Bondi. |
| 1937 | P 7 | Birch, Arthur John, M.Sc., D.Phil. <i>Oxon.</i> , The University Chemical Laboratory, Cambridge, England. |
| 1916 | | Birrell, Septimus, 17 Appian Way, Burwood. |
| 1920 | | Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 26A Wolseley-road, Mosman. |
| 1939 | P 3 | Blake, George Gascoigne, M.I.E.E., F.Inst.P., "Holmleigh," Cecil-avenue, Pennant Hills. |
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| 1946 | | Blaschke, Ernst Herbert, 6 Illistron Flats, 63 Carrabella-street, Kirribilli. |
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| 1920 | P 9 | Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., "Hills and Dales," Mittagong. (President, 1935.) |
| 1939 | P 24 | Bosworth, Richard Charles Leslie, M.Sc., D.Sc. <i>Adel.</i> , Ph.D. <i>Camb.</i> , F.A.C.I., F.Inst.P., c/o C.S.R. Co. Ltd., Pyrmont; p.r. 41 Spencer-road, Killara. |
| 1948 | | Boyd, Eric Harold, B.A., B.Sc., Dip.Ed., F.P.S., The King's School, Parramatta. |
| 1948 | | Boyd, Joan, B.Sc. Hons. <i>Lond.</i> , Dip.Ed. <i>Lond.</i> , The King's School, Parramatta. |
| 1938 | | Breckenridge, Marion, B.Sc., Department of Geology, The University of Sydney; p.r. 19 Handley-avenue, Thornleigh. |
| 1949 | P 2 | Brewer, Roy, B.Sc. <i>Syd.</i> , Research Officer, Division of Soils, C.S.I.R.O.; p.r. Block 1, Section 56, O'Connor, Canberra, A.C.T. |
| 1946 | P 1 | Breyer, Bruno, M.D., Ph.D., M.A., F.A.C.I., Lecturer in Agricultural Chemistry, Faculty of Agriculture, University of Sydney, Sydney. |
| 1919 | P 1 | Briggs, George Henry, D.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville. |
| 1942 | | Brown, Desmond J., M.Sc. (<i>Syd.</i>), Ph.D. (<i>Lond.</i>), D.I.C., Department of Medical Chemistry, Australian National University, 183 Euston-road, London, N.W.1. |
| 1945 | | Brown, Norma Dorothy (Mrs.), B.Sc., Biochemist, 2 Macauley-street, Leichhardt. |
| 1941 | | Brown, Samuel Raymond, A.C.A. <i>Aust.</i> , 87 Ashley-street, Chatswood. |
| 1935 | P 7 | Browne, Ida Alison, D.Sc., Senior Lecturer in Palaeontology, University of Sydney. |
| 1913 | P 23 | †Browne, William Rowan, D.Sc., Reader in Geology, University of Sydney. (President, 1932.) |
| 1947 | | Buchanan, Gregory Stewart, B.Sc. (Hons.), Lecturer in Physical Chemistry, Sydney Technical College; p.r. 19 Ferguson-avenue, Thornleigh. |
| 1940 | | Buckley, Lindsay Arthur, B.Sc., 29 Abingdon-road, Roseville. |
| 1946 | | Bullen, Keith Edward, M.A., B.Sc. <i>N.Z.</i> , M.A. <i>Melb.</i> , Ph.D., Sc.D. <i>Camb.</i> , F.R.S., Professor of Applied Mathematics, University of Sydney, Sydney, N.S.W. |
| 1898 | | †Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. <i>Syd.</i> , F.R.A.C.S., "Radstoke," Elizabeth Bay. |
| 1926 | | Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney. |
| 1938 | P 2 | †Carey, Samuel Warren, D.Sc., Professor of Geology, University of Tasmania, Tasmania. |
| 1948 | | Carroll, Dorothy, B.A., B.Sc., Ph.D., D.I.C., Secretary, Linnean Society of New South Wales, Science House, 157 Gloucester-street, Sydney. |
| 1903 | P 5 | †Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W. |
| 1945 | | Carter, Harold Burnell, B.V.Sc., Officer-in-Charge, Wool Biology Laboratory, 17 Randle-street, Sydney. |
| 1944 | | Cavill, George William Kenneth, M.Sc., c/o Department of Organic Chemistry, The University, Liverpool, Great Britain. |
| 1913 | P 4 | †Challinor, Richard Westman, F.R.I.C., A.A.C.I., A.S.T.C., F.C.S.; p.r. 54 Drumalbyn-road, Bellevue Hill. (President, 1933.) |
| 1933 | | Chalmers, Robert Oliver, A.S.T.C., Australian Museum, College Street, Sydney. |
| 1940 | | Chambers, Maxwell Clark, B.Sc., c/o Coty (England) Ltd., 35-41 Hutchinson-street, Moore Park; p.r. 58 Spencer-road, Killara. |
| 1913 | P 21 | †Cheel, Edwin, 40 Queen-street, Ashfield. (President, 1931.) |
| 1935 | P 2 | Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich. |
| 1935 | | Clark, Sir Reginald Marcus, K.B.E., Central Square, Sydney. |
| 1938 | | Clune, Francis Patrick, Author and Accountant, 15 Prince's-avenue, Vacluse. |
| 1941 | | Cohen, Max Charles, B.Sc., 80 "St. James," Stanley-street, Sydney. |
| 1940 | | Cohen, Samuel Bernard, M.Sc., A.A.C.I., 74 Boundary-street, Roseville. |
| 1940 | P 2 | Cole, Edward Ritchie, B.Sc., 7 Wolsten-avenue, Turramurra. |
| 1940 | P 1 | Cole, Joyce Marie, B.Sc., 7 Wolsten-avenue, Turramurra. |
| 1948 | | Cole, Leslie Arthur, Company Executive, 21 Carlisle-street, Rose Bay. |
| 1940 | | Collett, Gordon, B.Sc., 27 Rogers-avenue, Haberfield. |
| 1948 | | Cook, Cyril Lloyd, M.Sc., 176 Ben Boyd-road, Neutral Bay. |
| 1946 | | Cook, Rodney Thomas, A.S.T.C., 10 Riverview-road, Fairfield. |
| 1920 | | Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney. |
| 1945 | | Coombes, Arthur Roylance, A.S.T.C. (Chem.), 14 Georges River-road, Croydon. |
| 1913 | P 5 | †Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery. |

Elected.

- 1933 Corbett, Robert Lorimer, Scot Chambers, Hosking-place, Sydney.
 1940 Cortis-Jones, Beverly, M.Sc., 62 William-street, Roseville.
 1919 Cotton, Frank Stanley, D.Sc., Research Professor in Physiology in the University of Sydney.
- 1909 P 7 ‡Cotton, Leo Arthur, M.A., D.Sc., 113 Queen's Parade East, Newport Beach. (President, 1929.)
 1941 P 1 Craig, David Parker, Ph.D., Chemistry Department, University College, Gower-street, London, W.C.1., England.
 1921 P 1 ‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
 1948 Cymerman, John, Ph.D., D.I.C., A.R.C.S., B.Sc., A.R.I.C., Lecturer in Organic Chemistry, University of Sydney.
- 1940 Dadour, Anthony, B.Sc., 25 Elizabeth-street, Waterloo.
 1919 P 2 de Beuzeville, Wilfred Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
 1906 ‡Dixson, Sir William, "Merridong," Gordon-road, Killara.
 1913 P 3 ‡Doherty, William M., F.R.I.C., F.A.C.I., 36 George-street, Marrickville.
 1928 Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
 1947 Downes, Alan Marchant, B.Sc. (Hons.), Grandview-avenue, Croydon, Victoria.
 1948 Doyle, Shirley Kathleen, B.Sc., Microbiologist to H. Jones & Co.; p.r. 74 Duntroon-avenue, Roseville.
- 1943 Dudgeon, William, Manager, Commonwealth Drug Co., 50-54 Kippax-street, Sydney.
 1937 P 14 Dulhunty, John Allan, D.Sc., Geology Department, University of Sydney; p.r. 40 Manning-road, Double Bay. (President, 1947.)
 1948 Dunlop, Bruce Thomas, B.Sc., Schoolteacher, 77 Stanhope-road, Killara.
 1924 Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
- 1934 P 49 Dwyer, Francis P. J., D.Sc., Lecturer in Chemistry, University of Sydney, Sydney.
- 1945 Eade, Ronald Arthur, B.Sc., 21 Steward-street, Leichhardt.
 1949 Eisinger, Erich, "Ing." Austria, 24 Cooper-street, Double Bay.
 1934 P 2 Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (President, 1940.)
 1949 Ellison, Dorothy Jean, M.Sc. (Hons.) N.Z., Science Teacher, Abbotsleigh, Wahroonga; p.r. 51 Tryon-road, Lindfield.
 1940 Emmerton, Henry James, B.Sc., 1 Rosedale-road, Gordon.
 1944 Erhart, John Charles, Chemical Engineer, c/o "Ciba" Coy., Basle, Switzerland.
 1908 ‡Esdaile, Edward William, 42 Hunter-street, Sydney.
 1935 Evans, Silvanus Gladstone, A.I.A.A. Lond., A.R.A.I.A., 6 Major-street, Coogee.
 1949 Everingham, Richard, 3 The Bastion, Castlecrag.
- 1909 P 7 ‡Fawsitt, Charles Edward, D.Sc., Ph.D., F.A.C.I., Emeritus Professor of Chemistry, 14A Darling Point-road, Edgecliff. (President, 1919.)
 1940 Finch, Franklin Charles, B.Sc., Kirby-street, Rydalmere, N.S.W.
 1940 Fisher, Robert, B.Sc., 3 Sackville-street, Maroubra.
 1933 Fletcher, Harold Oswald, Palæontologist, Australian Museum, College-street, Sydney.
 1949 Flinter, Basil Harold, 75 Elizabeth Bay-road, Elizabeth Bay.
 1949 Follett, Frank William, Managing Director, Adastra Airways Pty. Ltd.; p.r. 74 Hopetoun-avenue, Vacluse.
 1932 Forman, Kenn. P., M.I.Refr.E., Box 1822, G.P.O., Sydney.
 1905 ‡Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
 1940 Franki, Robert James Anning, B.Sc., 891 New South Head-road, Rose Bay.
 1943 Frederick, Robert Desider Louis, B.E., 1540 High-street, Malvern, Victoria.
 1940 Freney, Martin Raphael, B.Sc., Central Wool Testing House, 17 Randle-street, Sydney.
- 1944 P 2 Friend, James Alan, 16 Kelburn-road, Roseville.
 1945 Furst, Hellmut Friedrich, B.D.S. (Syd.), D.M.D. (Hamburg), Dental Surgeon, 158 Bellevue-road, Bellevue Hill.

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| 1948 | | Gardiner, Edward Carson, Electrical Engineer in Charge of Construction at the Captain Cook Graving Dock, for the Department of Works and Housing ; p.r. 39 Spencer-street, Rose Bay. |
| 1935 | P 2 | Garretty, Michael Duhan, D.Sc., 477 St. Kilda-road, Melbourne, S.C.2, Victoria. |
| 1939 | P 4 | Gascoigne, Robert Mortimer, Chemistry Department, University of Liverpool, England. |
| 1926 | | Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney ; p.r. "Wirruna," Belmore-avenue, Wollstonecraft. |
| 1942 | P 3 | Gibson, Neville Allan, M.Sc., A.R.I.C., Industrial Chemist, 217 Parramatta-road, Haberfield. |
| 1947 | | Gill, Naida Sugden (Miss), B.Sc., 45 Neville-street, Marrickville. |
| 1947 | | †Gill, Stuart Frederic, School Teacher, 45 Neville-street, Marrickville. |
| 1940 | | Gillis, Richard Galvin, Senior Lecturer, Organic Chemistry, Melbourne Technical College ; p.r. 4 Tennyson-avenue, Caulfield, S.E.7, Victoria. |
| 1948 | | Glasson, Kenneth Roderick, B.Sc., Geologist, Lake George Mines Ltd., Captain's Flat, N.S.W. |
| 1945 | | Goddard, Roy Hamilton, F.C.A. Aust., Royal Exchange, Bridge-street, Sydney. |
| 1947 | | Goldsworthy, Neil Ernest, M.B., Ch.M. Syd., Ph.D., D.T.M. & H. Camb., D.T.M. & H. Eng., D.P.H. Camb., 65 Roseville-avenue, Roseville. |
| 1949 | | Gordon, William Fraser, B.Sc. Syd., Industrial Chemist ; p.r. 176 Avoca-street, Randwick. |
| 1936 | | Goulston, Edna Maude, B.Sc., 83 Birriga-road, Bellevue Hill. |
| 1949 | | Gover, Alfred Terence, M.Com., 32 Benelong-road, Cremorne. |
| 1948 | | Gray, Charles Alexander Menzies, B.Sc., B.E., 75 Woniara-road, Hurstville. |
| 1938 | | Griffiths, Edward L., B.Sc., A.A.C.I., A.R.I.C., Chief Chemist, Department of Agriculture ; p.r. 151 Wollongong-road, Arncliffe. |
| 1946 | P 1 | Gutmann, Felix, Ph.D., F.Inst.P., M.I.R.E., N.S.W. University of Technology, Broadway, Sydney. |
| 1948 | P 4 | Gyarfas, Eleonora Clara, M.Sc. Budapest, Research Assistant, University of Sydney ; p.r. 53 Simpson-street, Bondi. |
| 1947 | | Hall, Lennard Robert, B.Sc., Geological Survey, Department of Mines, Bridge-street, Sydney. |
| 1934 | | Hall, Norman Frederick Blake, M.Sc., Chemist, 15A Wharf-road, Longueville. |
| 1892 | | †Halloran, Henry Ferdinand, L.S., A.M.I.E.Aust., F.S.I.Eng., M.T.P.I.Eng., 153 Elizabeth-street, Sydney ; p.r. 23 March-street, Bellevue Hill. |
| 1949 | | Hampton, Edward John William, A.S.T.C. ; p.r. 1 Hunter Street, Waratah, N.S.W. |
| 1940 | P 14 | Hanlon, Frederick Noel, B.Sc., Geologist, Department of Mines, Sydney. |
| 1905 | P 6 | †Harker, George, D.Sc., F.A.C.I. ; p.r. 89 Homebush-road, Strathfield. |
| 1936 | | Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., National Standards Laboratory, University Grounds, City-road, Chippendale. |
| 1934 | | Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo. |
| 1948 | P 1 | Harris, Clive Melville, A.S.T.C., Demonstrator, Chemistry Department, Sydney Technical College ; p.r. 12 Livingstone-road, Lidcombe. |
| 1949 | | Harris, Henry Maxwell, B.Sc., B.E., Assistant Engineer, W.C. & I.C., 25 Prospect-road, Summer Hill. |
| 1946 | | Harrison, Ernest John Jasper, B.Sc., Geologist, N.S.W. Geological Survey, Department of Mines, Sydney. |
| 1934 | | Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c.o. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord ; p.r. 34 Nicholson-street, Chatswood. |
| 1919 | | Henriques, Frederick Lester, 208 Clarence-street, Sydney. |
| 1945 | | Higgs, Alan Charles, Manager, Asbestos Products Pty. Ltd. ; p.r. corner Bungalow-avenue and New-street, Balgowlah. |
| 1938 | P 4 | Hill, Dorothy, M.Sc. Q'ld., Ph.D. Cantab., Geological Research Fellow, University of Queensland, Brisbane. |
| 1936 | | Hirst, Edward Eugene, A.M.I.E., Vice-Chairman and Joint Managing Director, British General Electric Co. Ltd. ; p.r. "Springmead," Ingleburn. |
| 1928 | | Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (Aust.), "St. Cloud," Beaconsfield-road, Chatswood. |
| 1948 | P 3 | Hogarth, Julius William, 8 Jeanneret-avenue, Hunter's Hill. |
| 1916 | | Hoggan, Henry James, A.M.I.M.E. Lond., A.M.I.E. Aust., Consulting and Designing Engineer, 81 Frederick-street, Rockdale. |
| 1941 | | Howard, Harold Theodore Clyde, B.Sc., Principal, Technical College, Granville. |

Elected.

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| 1938 | P 12 | Hughes, Gordon Kingsley, B.Sc., Department of Chemistry, University of Sydney, Sydney. |
| 1947 | P 1 | Humpoletz, Justin Ernst, B.Sc. <i>Syd.</i> , 21 Belgium-avenue, Roseville. |
| 1923 | P 3 | †Hynes, Harold John, D.Sc., B.Sc.Agr., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville. |
| 1943 | | Iredale, Thomas, D.Sc., F.R.I.C., Chemistry Department, University of Sydney, p.r. 96 Roseville-avenue, Roseville. |
| 1942 | P 1 | Jaeger, John Conrad, M.A., D.Sc., University of Tasmania, Hobart, Tasmania. |
| 1909 | P 15 | Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.) |
| 1949 | | Joklik, Gunther F., B.Sc., c.o. Bureau of Mineral Resources, Canberra, A.C.T. |
| 1935 | P 6 | Joplin, Germaine Anne, B.Sc., Ph.D., 18 Wentworth-street, Eastwood. |
| 1948 | P 1 | Jopling, Alan Victor, B.Sc., B.E., 28 Cliff-street, Manly. |
| 1930 | | Judd, William Percy, 123 Wollongong-road, Arncliffe. |
| 1935 | | Kelly, Caroline Tennant (Mrs.), Dip.Anth., "Eight Bells," Cast Hill. |
| 1940 | | Kennard, William Walter, 9 Bona Vista-avenue, Maroubra. |
| 1924 | P 1 | Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield. |
| 1934 | | Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, 29 Nundah-street, Lane Cove. |
| 1948 | | Kimble, Frank Oswald, Engineer, 16 Evelyn-avenue, Concord. |
| 1943 | | Kimble, Jean Annie, B.Sc., Research Chemist, 383 Marrickville-road, Marrickville. |
| 1920 | | Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. 18 Lyne-road, Cheltenham. |
| 1948 | | Knight, Oscar Le Maistre, B.E. <i>Syd.</i> , A.M.I.C.E., A.M.I.E.Aust., Engineer, 10 Mildura-street, Killara. |
| 1948 | | Koch, Leo E., Ph.D., D.Sc. (<i>Cologne</i>), Department of Geology, The University of Sydney; p.r. 39 Bond-street, Mosman. |
| 1939 | P 1 | Lambeth, Arthur James, B.Sc., "Naranje," Swæthaven-road, Wetherill Park, N.S.W. |
| 1949 | | Lancaster, Kelvin John, B.Sc., 43 Balfour-road, Ross Bay. |
| 1936 | | Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., British Australian Lead Manufacturers Pty. Ltd., Box 21, P.O., Concord. |
| 1946 | | Lederer, Michael, 67 Edgecliff-road, Bondi Junction. |
| 1947 | | Le Fevre, Raymond James Wood, D.Sc., Ph.D., F.R.I.C., Professor of Chemistry, Chemistry Department, University of Sydney, Sydney. |
| 1936 | P 2 | Lemberg, Max Rudolph, D.Phil., Institute of Medical Research, Royal North Shore Hospital, St. Leonards. |
| 1920 | | Le Souef, Albert Sherbourne, 3 Silex-road, Mosman. |
| 1929 | P 56 | †Lions, Francis, B.Sc., Ph.D., A.R.I.C., Reader, Department of Chemistry, University of Sydney. (President, 1946-47.) |
| 1942 | | Lippmann, Arthur S., M.D., 175 Macquarie-street, Sydney. |
| 1947 | | Lloyd, James Charles, B.Sc. <i>Syd.</i> , N.S.W. Geological Survey, 41 Goulburn-street, Liverpool. |
| 1940 | P 1 | Lockwood, William Hutton, B.Sc., c.o. Institute of Medical Research, The Royal North Shore Hospital, St. Leonards. |
| 1906 | | †Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney. |
| 1949 | | Loughnan, Frederick Charles, "Bodleian", 26 Kenneth-street, Longueville. |
| 1947 | | Lowenbein, Gladys Olive (Mrs.), B.Sc. <i>Melb.</i> , F.R.I.C. <i>Gt. B.</i> , A.A.C.I., Director of Research, Australian Leather Research Association; p.r. 5 Berrima Flats, 12 Mulwarrie-avenue, Randwick. |
| 1943 | | †Luber, Daphne (Mrs.), B.Sc., 98 Lang-road, Centennial Park. |
| 1945 | | Luber, Leonard, Pharmacist, 80 Queen-street, Woollahra. |
| 1948 | P 2 | Lyons, Lawrence Ernest, B.A., M.Sc., Lecturer in Chemistry, The University of Sydney; p.r. 13 Albert-road, Strathfield. |
| 1942 | | Lyons, Raymond Norman Matthew, M.Sc., Biochemical Research Worker, |

Elected.

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| 1939 | P 4 | Maccoll, Allan, M.Sc., Department of Chemistry, University College, Gower-street, London, W.C.1. |
| 1949 | | McCarthy, Frederick David, Curator of Anthropology, Australian Museum, Sydney; p.r. 10 Tycannah-road, Northbridge. |
| 1943 | | McCoy, William Kevin, Analytical Chemist, c/o Mr. A. J. McCoy, 39 Malvern-avenue, Merrylands. |
| 1949 | | McElroy, Clifford Turner, 147 Arden-street, Coogee. |
| 1940 | | McGregor, Gordon Howard, 4 Maple-avenue, Pennant Hills. |
| 1948 | | McInnes, Gordon Elliott, Department of Geology, The University of Sydney; p.r. 46 Laycock-street, Bexley. |
| 1906 | P 2 | †McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville. |
| 1944 | P 7 | McKenzie, Hugh Albert, B.Sc., 52 Bolton-street, Guildford. |
| 1943 | P 1 | McKern, Howard Hamlet Gordon, A.S.T.C., A.A.C.I., Assistant Chemist, Museum of Technology and Applied Science, Harris-street, Ultimo; p.r. Flat 2, 42A, Waimea-street, Burwood. |
| 1947 | | McMahon, Patrick Reginald, M.Agr.sc. N.Z., Ph.D. Leeds, A.R.I.C., A.N.Z.I.C., Lecturer-in-charge, Sheep and Wool Department, Sydney Technical College, East Sydney. |
| 1927 | | McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W. |
| 1943 | | McNamara, Barbara Joyce (Mrs.), M.B., B.S., Yeoval, 7.W. |
| 1946 | | McPherson, John Charters, 14 Sarnar-road, Greenwich. |
| 1946 | P 1 | McRoberts, Helen May, B.Sc., New England University College, Armidale. |
| 1947 | | Magee, Charles Joseph, D.Sc.Agr. Syd., M.Sc. Wis., Chief Biologist, Department of Agriculture; p.r. 4 Alexander-parade, Roseville. |
| 1947 | | Maley, Leo Edmund, M.Sc., B.Sc. (Hons.), A.A.C.I., A.M.A.I.M.M., 116 Maitland road, Mayfield. |
| 1940 | | Malone, Edward E., 33 Windsor-road, St. Mary's. |
| 1947 | P 12 | Mapstone, George E., M.Sc., A.A.C.I., M.Inst.Pet., Chief Chemist of National Oil Pty. Ltd., Glen Davis; p.r. 2 Anderson Square, Glen Davis, N.S.W. |
| 1949 | | Marshall, Charles Edward, Ph.D., D.Sc., Professor of Geology, The University of Sydney, Sydney. |
| 1944 | | Martin, Cyril Maxwell, Chemist, 22 Wattle-street, Haberfield. |
| 1946 | | May, Albert, Ph.D., M.A., 94 Birriga-road, Bellevue Hill. |
| 1935 | P 1 | Maze, William Harold, M.Sc., Registrar, The University of Sydney, Sydney. |
| 1949 | | Meares, Harry John Devenish, Technical Librarian, Colonial Sugar Refining Co. Ltd., Box 483, G.P.O., Sydney. |
| 1912 | † | Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Fairlight. |
| 1929 | P 25 | Mellor, David Paver, D.Sc., F.A.C.I., Reader, Department of Chemistry, University of Sydney; p.r. 137 Middle Harbour-road, Lindfield. (President, 1941-42.) |
| 1928 | | Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, Jordan House, Jordan Terrace, Bowen Hills, Brisbane. |
| 1940 | | Millership, William, M.Sc., Chief Chemist, Davis Gelatine (Aust.) Pty. Ltd., 15 Shaw-avenue, Earlwood. |
| 1922 | P 28 | Morrison, Frank Richard, A.A.C.I., F.C.S., Deputy Director, Museum of Technology and Applied Science, Harris-street, Ultimo. |
| 1941 | | Morrissey, Matthew John, B.A., A.S.T.C., Auburn Street, Parramatta. |
| 1934 | | Mort, Francis George Arnot, A.A.C.I., Chemist, 110 Green's-road, Fivedock. |
| 1948 | | Mosher, Kenneth George, B.Sc., Geologist, c.o. Joint Coal Board, 66 King-street, Sydney. |
| 1944 | | Moye, Daniel George, Geologist, 6 First-avenue, Snowy Mountains Hydro-Electric Authority, Cooma, N.S.W. |
| 1946 | | Mulholland, Charles St. John, B.Sc., Geologist, Department of Mines, Sydney. |
| 1948 | | Mulley, Joan W., Technical Officer, C.S.I.R.; p.r. 4 Billyard-avenue, Elizabeth Bay. |
| 1915 | † | Murphy, Robert Kenneth, Dr.Eng., Chem., A.S.T.C., M.I.Chem.E., F.A.C.I., Principal, Sydney Technical College, Sydney. |
| 1923 | P 2 | Murray, Colonel Jack Keith, B.A., B.Sc.Agr., Administrator, Territory of Papua-New Guinea, Government House, Port Moresby. |
| 1948 | | Naylor, Betty Yvonne, B.Sc., 6 Niblick-avenue, Roseville. |
| 1930 | P 7 | Naylor, George Francis King, M.A., M.Sc., Dip.Ed., A.A.I.I.P., Lecturer in Philosophy and Psychology, University of Queensland, Brisbane, Qld. |
| 1943 | | Neuhaus, John William George, 190 Old Prospect-road, Wentworthville. |
| 1932 | | Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Professor of Botany, The University of Ceylon, Colombo, Ceylon. |

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| 1943 | | Nicol, Alexander Campbell, A.S.T.C., A.A.C.I., Chief Chemist, Crown Crystal Glass Co.; p.r. 200 Paine-street, Maroubra. |
| 1935 | | Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown. |
| 1945 | P 1 | Noakes, Lyndon Charles, Geologist, c/o Mineral Resources Survey, Canberra, A.C.T. |
| 1938 | P 1 | Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., c/o C.S.I.R., 314 Albert-street, East Melbourne, Vic. |
| 1920 | P 4 | †Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Under Secretary, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (President, 1934.) |
| 1947 | | Nordon, Peter, A.S.T.C., A.A.C.I., Chemical Engineer, 39 Tahlee-street, Burwood. |
| 1948 | | Northcott, Jean, B.Sc. (Hons.), Chemistry Department, The University of Sydney; p.r. 38 Canberra-street, Lane Cove. |
| 1940 | P 25 | Nyholm, Ronald Sydney, M.Sc., Chemistry Department, University College, Gower-street, London, W.C.1, England. |
| 1935 | P 4 | O'Connell, Rev. Daniel J. K., S.J., M.Sc., D.Ph., F.R.A.S., Riverview College Observatory, Sydney. |
| 1947 | | Old, Adrian Noel, B.Sc.Agr., Chemist, Department of Agriculture; p.r. 4 Springfield-avenue, Pott's Point. |
| 1921 | P 11 | Osborne, George Davenport, D.Sc. Syd., Ph.D. Camb., Lecturer and Demonstrator in Geology in the University of Sydney. (President, 1944.) |
| 1920 | P 75 | Penfold, Arthur Ramon, F.A.C.I., F.C.S., Director, Museum of Technology and Applied Science, Harris-street, Ultimo. (President, 1931.) |
| 1949 | | Penrose, Ruth Elizabeth, B.Sc., 92 Baringa-road, Northbridge. |
| 1948 | | Perry, Hubert Roy, B.Sc., 74 Woodbine-street, Bowral. |
| 1938 | | Phillips, Marie Elizabeth, B.Sc., Botany Department, University, Manchester, 13, England. |
| 1935 | | Phillips, Orwell, 55 Darling Point-road, Edgecliff. |
| 1946 | | Pinwell, Norman, B.A. (Q'land), The Scots College, Bellevue Hill. |
| 1943 | P 1 | Plowman, Ronald Arthur, B.Sc. Lond., A.S.T.C., A.A.C.I., Analytical Chemist, 21 Harris-street, Normanhurst. |
| 1919 | | Poate, Hugh Raymond Guy, M.B., Ch.M. Syd., F.R.C.S. Eng., L.R.C.P. Lond., F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill. |
| 1949 | | Poggendorff, Walter Hans George, B.Sc.Agr., Chief of the Division of Plant Industry, N.S.W. Department of Agriculture, Box 36A, G.P.O., Sydney. |
| 1896 | | †Pope, Roland James, B.A. Syd., M.D., Ch.M., F.R.C.S. Edin., 185 Macquarie-street, Sydney. |
| 1946 | | Potter, Bryce Harrison, B.Sc. (Hons.) Syd., 68 Wharf-road, Gladesville. |
| 1921 | P 2 | Powell, Charles Wilfrid Roberts, F.R.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman. |
| 1938 | | Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern. |
| 1945 | | Prescott, Alwyn Walker, B.Eng., Lecturer in Mechanical and Electrical Engineering in the University of Sydney; p.r. Harris-road, Normanhurst. |
| 1927 | | Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 8 Wattle-street, Killara. |
| 1918 | P 1 | Priestley, Henry, M.D., Ch.M., B.Sc., 54 Fuller's-road, Chatswood. (President, 1942-43.) |
| 1945 | | Proud, John Seymour, Mining Engineer, 4 View-street, Chatswood. |
| 1893 | | †Purser, Cecil, B.A., M.B., Ch.M. Syd., "Ascot," Grosvenor-road, Wahroonga. |
| 1935 | P 3 | †Quodling, Florrie Mabel, B.Sc., Lecturer in Geology, University of Sydney |
| 1922 | P 6 | Raggatt, Harold George, D.Sc., Director, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, C.1, Victoria. |
| 1940 | P 2 | Ralph, Colin Sydney, B.Sc., 24 Canberra-street, Epping. |
| 1919 | P 3 | Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., 57, William-street, Sydney. |
| 1936 | | Randall, Harry, Buena Vista-avenue, Denistone. |
| 1947 | | Ray, Nancy Evelyn (Mrs.), Plastics Manufacturer, 14 Hedger-avenue, Ashfield. |

Elected.

- 1947 Ray, Reginald John, Plastics Manufacturer and Research Chemist, 14 Hedger-avenue, Ashfield.
- 1931 P 1 Rayner, Jack Maxwell, B.Sc., F.Inst.P., Chief Geophysicist, Bureau of Mineral Resources, Geology and Geophysics, 485 Bourke-street, Melbourne, Vic.
- 1935 Reid, Cicero Augustus, 19 Newton-road, Strathfield.
- 1947 Reuter, Fritz Henry, Ph.D. (*Berlin*, 1930), F.A.C.I., 94 Onslow-street, Rose Bay.
- 1946 Rhodes-Smith, Cecil, 261 George-street, Sydney.
- 1947 Ritchie, Arthur Sinclair, A.S.T.C., Lecturer in Mineralogy and Geology, Newcastle Technical College; p.r. 188 St. James-road, New Lambton, N.S.W.
- 1947 Ritchie, Bruce, B.Sc. (Hons.), c/o Pyco Products Pty. Ltd., 576 Parramatta-road, Petersham.
- 1939 P 18 Ritchie, Ernest, M.Sc., Senior Lecturer, Chemistry Department, University of Sydney, Sydney.
- 1939 P 3 Robbins, Elizabeth Marie (Mrs.), M.Sc., 344 Railway-parade, Guildford.
- 1933 Roberts, Richard George Crafter, Electrical Engineer, c/o C. W. Stirling & Co., Asbestos House, York and Barrack-streets, Sydney.
- 1940 Robertson, Rutherford Ness, B.Sc. *Syd.*, Ph.D. *Cantab.*, Senior Plant Physiologist, C.S.I.R., Division of Food Preservation, Private Bag, P.O., Homebush; p.r. Flat 4, 43 Johnston-street, Annandale.
- 1949 P 3 Robertson, William Humphrey, B.Sc., Astronomer, Sydney Observatory, Sydney.
- 1935 P 2 Room, Thomas G., M.A., F.R.S., Professor of Mathematics in the University of Sydney.
- 1940 Rosenbaum, Sidney, 44 Gilderthorp-avenue, Randwick.
- 1948 Rosenthal-Schneider, Ilse, Ph.D., 48 Cambridge-avenue, Vaucluse.
- 1940 Ross, Jean Elizabeth, B.Sc., Dip.Ed., 5 Stanton-road, Haberfield.
- 1948 Ross, Leonard Paul, B.Sc., 137 Burwood-road, Enfield.
- 1945 Rountree, Phyllis Margaret, M.Sc. *Melb.*, Dip.Bact. *Lond.*, Royal Prince Alfred Hospital, Sydney.
- 1945 Sampson, Aileen (Mrs.), sc.Dip. (A.S.T.C., 1944), 9 Knox-avenue, Epping.
- 1920 Scammell, Rupert Boswood, B.Sc. *Syd.*, A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern; p.r. 10 Buena Vista-avenue, Clifton Gardens.
- 1948 P 1 Schafer, Harry Neil Scott, B.Sc., 18 Bartlett-street, Summer Hill.
- 1946 P 1 Scott, Beryl (Miss), B.Sc., Geology Department, University of Tasmania.
- 1940 Scott, Reginald Henry, B.Sc., 3 Walbundry-avenue, East Kew, Victoria.
- 1949 See, Graeme Thomas, Analytical Chemist, -2 Skipton Flats, corner Mount and Dudley-streets, Coogee.
- 1933 Selby, Esmond Jacob, Dip.Com., Sales Manager, Box 175 D, G.P.O., Sydney.
- 1936 Sellenger, Brother Albertus, St. Ildephonsus College, New Norcia, W.A.
- 1948 †Sharp, Kenneth Raeburn, Geology Department, The University of Sydney; p.r. Kitchener-road, St. Ives.
- 1938 Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, c/o Shell Co. of Aust., North Terrace, Adelaide.
- 1936 P 2 Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. *Melb.*, 43 Robertson-road, Centennial Park.
- 1948 Sherwood, Ian Russell, D.Sc., F.A.C.I., Research Bacteriologist, Research Laboratory, Colonial Sugar Refining Co. Ltd., John-street, Pyrmont.
- 1945 Shulman, Albert, B.Sc., Industrial Chemist, Flat 2, Linden Court, Linden-avenue, Woollahra.
- 1945 P 3 Simmons, Lewis Michael, B.Sc. (Hons.) *Lond.*, Ph.D. *Lond.*, F.A.C.I., Head of Science Department, Scots College; p.r. The Scots College, Victoria-road, Bellevue Hill.
- 1948 Simonett, David Stanley, B.Sc., Geography Department, The University of Sydney; p.r. 14 Selwyn-street, Artarmon.
- 1943 Simpson, John Kenneth Moore, Industrial Chemist, "Browie," Old Castle Hill-road, Castle Hill.
- 1933 Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Pty. Ltd., Manufacturing Chemists, Mandemar-avenue, Homebush; p.r. "Raiatea," Oyama-avenue, Manly.
- 1940 Smith, Eric Brian Jeffcoat, 1 Rocklands-road, Wollstonecraft.
- 1947 Smith-White, William Broderick, M.A. *Cantab.*, B.Sc. *Syd.*, Department of Mathematics, University of Sydney; p.r. 28 Cranbrook-avenue, Cremorne.
- 1919 Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.

Elected.

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| 1949 | | Stanton, Richard Limon, B.Sc., Teaching Fellow in Geology, The University of Sydney, Sydney; p.r. 42 Hopetoun-avenue, Mosman. |
| 1916 | | Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney. |
| 1914 | | †Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney; p.r. Captain Piper's-road and New South Head-road, Vaucluse. |
| 1948 | P 1 | Stevens, Neville Cecil, B.Sc., Geology Department, The University of Sydney; p.r. 12 Salisbury-street, Hurstville. |
| 1900 | P 1 | †Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Emeritus Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.) |
| 1942 | | Still, Jack Leslie, B.Sc., Ph.D., Professor of Biochemistry, The University of Sydney, Sydney. |
| 1916 | P 1 | Stone, Walter George, F.S.T.C., F.A.C.I., Chief Analyst, Department of Mines, Sydney; p.r. 26 Rosslyn-street, Bellevue Hill. |
| 1918 | | †Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield. |
| 1919 | | †Sutherland, George Fife, A.R.C.Sc. <i>London</i> , 47 Clanwilliam-street, Chatswood. |
| 1920 | | Sutton, Harvey, O.B.E., M.D., D.P.H. <i>Melb.</i> , B.Sc. <i>Oxon.</i> , Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay. |
| 1941 | P 2 | Swanson, Thomas Baikie, M.Sc. <i>Adel.</i> , c/o Technical Service Department, ICIanz, Box 1911, G.P.O., Melbourne, Victoria. |
| 1948 | | Swinbourne, Ellice Simmons, Organic Chemist, A.S.T.C., A.A.C.I., 1 Raglan-street, Manly. |
| 1915 | P 3 | †Taylor, Brigadier Harold B., M.C., D.Sc., F.R.I.C., F.A.C.I., Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 12 Wood-street, Manly. |
| 1944 | | Thomas, Andrew David, Squadron Leader, R.A.A.F., M.Sc., A.Inst.P. 17 Millicent-avenue, Toorak, Melbourne, E.2., Vic. |
| 1946 | | Thomas, Ifor Morris, M.Sc., Department of Zoology, University of Adelaide, Adelaide, S.A. |
| 1946 | P 1 | Thompson, Nora (Mrs.), B.Sc. <i>Syd.</i> , c/o Australasian Petroleum Coy., Port Moresby, Papua. |
| 1919 | | Thorne, Harold Henry, M.A. <i>Cantab.</i> , B.Sc. <i>Syd.</i> , F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft. |
| 1935 | | Tommerup, Eric Christian, M.Sc., A.A.C.I., Queensland Agricultural College, Lawes, via Brisbane, Queensland. |
| 1923 | | Toppin, Richmond Douglas, A.R.I.C., 51 Crystal-street, Petersham. |
| 1940 | | Tow, Aubrey James, M.Sc., No. 5, "Werrington," Manion-avenue, Rose Bay. |
| 1949 | | Trebeck, Prosper Charles Brian, A.C.I.S., F.Com.A., <i>Eng.</i> , A.F.I.A., A.A.A., J.P., 3 Honda-road, Neutral Bay. |
| 1943 | | Turner, Ivan Stewart, M.A., M.Sc., Ph.D., Lecturer in Mathematics, University of Sydney; p.r. 120 Awaba-street, Mosman. |
| 1949 | | Vallance, Thomas George, 57 Auburn-street, Sutherland. |
| 1921 | | Vicars, Robert, Marrickville Woollen Mills, Marrickville. |
| 1935 | | Vickery, Joyce Winifred, M.Sc., Botanic Gardens, Sydney; p.r. 17 The Promenade, Cheltenham. |
| 1933 | P 5 | Voisey, Alan Heywood, D.Sc., Lecturer in Geology and Geography, New England University College, Armidale. |
| 1903 | P 10 | †Vonwiller, Oscar U., B.Sc., F.Inst.P., Emeritus Professor of Physics in the University of Sydney; p.r. "Eightbells," Old Castle Hill-road, Castle Hill. (President, 1930.) |
| 1948 | | Walker, Donald Francis, Surveyor, 13 Beauchamp-avenue, Chatswood. |
| 1943 | | Walker, James Foote, Company Secretary, 11 Brucedale-avenue, Epping. |
| 1919 | P 2 | Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney; p.r. 45 Nelson-road, Killara. (Member from 1910-1913. President, 1943-44.) |
| 1913 | P 5 | †Wardlaw, Hy. Sloane Halcro, D.Sc. <i>Syd.</i> , F.A.C.I., c/o Kanematsu Institute, Sydney Hospital, Macquarie Street, Sydney. (President, 1939.) |
| 1944 | | Warner, Harry, A.S.T.C., Chemist, 6 Knibbs-street, Turner, Canberra, A.C.T. |
| 1921 | | †Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., c/o Mrs. Millett Illoura-avenue, Wahroonga. |
| 1919 | P 1 | Waterhouse, Lionel Lawry, B.E. <i>Syd.</i> , Lecturer and Demonstrator in Geology in the University of Sydney. |

Elected.

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|------|------|---|
| 1919 | P 7 | Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Research Professor of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (President, 1937.) |
| 1944 | | Watkins, William Hamilton, B.Sc., Industrial Chemist, 57 Bellevue-street, North Sydney. |
| 1911 | P 1 | †Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vacluse. (President, 1925.) |
| 1921 | | Watts, Arthur Spencer, "Araboono", Glebe-street, Randwick. |
| 1947 | | Webb, Gordon Keyes, A.F.I.A., A.C.I.S., Accountant, c/o Max Wurcker (1930) Pty. Ltd., 99 York-street, Sydney. |
| 1921 | | Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney. |
| 1947 | | Werner, Ronald Louis, Industrial Chemist, 25 Dine-street, Randwick. |
| 1949 | | Westheimer, Gerald, B.Sc., F.S.T.C., F.I.O., Optometrist, 727 George-street, Sydney. |
| 1946 | | Weston, Margaret Crowley, B.A., 41 Bulkara-road, Bellevue Hill. |
| 1943 | | Whiteman, Reginald John Nelson, M.B., Ch.M., F.R.A.C.S., 143 Macquarie-street, Sydney. |
| 1928 | | Wiesoner, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, Bram Hall, Jersey-road, Strathfield. |
| 1949 | | Williams, Benjamin, A.S.T.C., 97 McMichael-street, Maryville, N.S.W. |
| 1942 | | Williams, Gordon Roy, B.Sc. |
| 1949 | | Williamson, William Harold, Hughes-avenue, Ermington. |
| 1945 | | Willis, Jack Lohane, B.Sc., Flat 5, "Naroona", Hampden-street, North Sydney. |
| 1943 | | Winch, Leonard, B.Sc., 26 Boonah-street, Griffith, N.S.W. |
| 1940 | | Wogan, Samuel James, Range-road, Sarina, North Queensland. |
| 1936 | P 9 | Wood, Harley Weston, M.Sc., A.Inst.P., F.R.A.S., Government Astronomer, Sydney Observatory, Sydney. (President, 1949.) |
| 1906 | P 12 | †Woolnough, Walter George, D.Sc., F.G.S., c/o Mr. W. L. Woolnough, "Callabonna", 8 Park-avenue, Gordon. |
| 1916 | | Wright, George, Company Director, c/o Hector Allen, Son & Morrison, 7 Wynyard-street, Sydney. |
| 1946 | | Wyndham, Norman Richard, M.D., M.S. (Syd.), F.R.C.S. (Eng.), F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney. |
| 1948 | | Zingel, Judith, B.Sc., Geology Department, The University of Sydney, Sydney. |

HONORARY MEMBERS.

Limited to Twenty.

Elected.

| | | |
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| 1949 | | Burnet, Frank Macfarlane, M.D., Ph.D., F.R.S., Director of the Walter and Eliza Hall Research Institute, Melbourne. |
| 1949 | | Florey, Sir Howard, M.B., B.S., B.Sc., M.A., Ph.D., F.R.S., Professor of Pathology, Oxford University, England. |
| 1914 | | Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England. |
| 1946 | | Jones, Sir Harold Spencer, M.A., D.Sc., F.R.S., Astronomer Royal, Royal Observatory, Greenwich, London, S.E.10. |
| 1915 | | Maitland, Andrew Gibb, F.G.S., "Bon Accord," 28 Melville-terrace, South Perth, W.A. |
| 1912 | | Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England. |
| 1948 | | Oliphant, Marcus L., B.Sc., Ph.D., F.R.S., Professor of Physics, The University, Edgbaston, Birmingham 15, England. |
| 1948 | | Robinson, Sir Robert, M.A., D.Sc., F.C.S., F.I.C., F.R.S., Professor of Chemistry, Oxford University, England. |
| 1946 | | Wood-Jones, F., D.Sc., M.B., B.S., F.R.C.S., L.R.C.P. (Lond.), F.R.S., F.Z.S., Professor of Anatomy, University of Manchester, England. |

OBITUARY, 1949-50.

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|------|------------------------|
| 1890 | Henry Harvey Dare. |
| 1916 | Walter John Enright. |
| 1879 | Joseph Foreman. |
| 1891 | Robert Thomas McKay. |
| 1941 | Dansie Thomas Sawkins. |
| 1909 | Charles Josiah White. |

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke "as a learned colonist, a faithful minister of religion, and an eminent scientific man." It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public, and of a medal to be given from time to time for distinguished work in the Natural Sciences done in or on the Australian Commonwealth and its territories; the person to whom the award is made may be resident in the Australian Commonwealth or its territories, or elsewhere.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. "The Volcanoes of Victoria," and "The Origin of Dolomite" (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.
1907. "Geography of Australia in the Permo-Carboniferous Period" (two lectures). By Professor T. W. E. David, B.A., F.R.S.
- "The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.
- "Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.
- "The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.
1918. "Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.
1919. "Geology at the Western Front," By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.
1936. "The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (THIS JOURN., 1936, 70, 39.)
1937. "Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (THIS JOURN., 1937, 71, 68.)
1938. "The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (THIS JOURN., 1938, 71, 503.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S. (THIS JOURN., 1939, 73, 41.)
1940. "The Geologist and Sub-surface Water." By E. J. Kenny, M.Aust.I.M.M. (THIS JOURN., 1940, 74, 283.)
1941. "The Climate of Australia in Past Ages." By C. A. Sussmilch, F.G.S. (THIS JOURN., 1941, 75, 47.)
1942. "The Heroic Period of Geological Work in Australia." By E. C. Andrews, B.Sc.
1943. "Australia's Mineral Industry in the Present War." By H. G. Raggatt, D.Sc.
1944. "An Australian Geologist Looks at the Pacific." By W. H. Bryan, M.C., D.Sc.
1945. "Some Aspects of the Tectonics of Australia." By Professor E. S. Hills, D.Sc., Ph.D.
1946. "The Pulse of the Pacific." By Professor L. A. Cotton, M.A., D.Sc.
1947. "The Teachers of Geology in Australian Universities." By Professor H. S. Summers D.Sc.
1948. "The Sedimentary Succession of the Bibliando Dome: Record of a Prolonger Proterozoic Ice Age." By Sir Douglas Mawson, O.B.E., F.R.S., D.Sc., B.E.
1949. "Metallogenetic Epochs and Ore Regions in Australia." By W. R. Browne, D.Sc.

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.

- 1878 *Professor Sir Richard Owen, K.C.B., F.R.S.
- 1879 *George Bentham, C.M.G., F.R.S.
- 1880 *Professor Thos. Huxley, F.R.S.
- 1881 *Professor F. M'Coy, F.R.S., F.G.S.
- 1882 *Professor James Dwight Dana, LL.D.
- 1883 *Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
- 1884 *Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.

Awarded.

- 1885 *Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
 1886 *Professor L. G. De Koninck, M.D.
 1887 *Sir James Hector, K.C.M.G., M.D., F.R.S.
 1888 *Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
 1889 *Robert Lewis John Ellery, F.R.S., F.R.A.S.
 1890 *George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
 1891 *Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
 1892 *Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
 1893 *Professor Ralph Tate, F.L.S., F.G.S.
 1895 *Robert Logan Jack, LL.D., F.G.S., F.R.G.S.
 1895 *Robert Etheridge, Jnr.
 1896 *The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
 1900 *Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
 1901 *Edward John Eyre.
 1902 *F. Manson Bailey, C.M.G., F.L.S.
 1903 *Alfred William Howitt, D.Sc., F.G.S.
 1907 *Professor Walter Howchin, F.G.S., University of Adelaide.
 1909 *Dr. Walter E. Roth, B.A.
 1912 *W. H. Twelvetrees, F.G.S.
 1914 Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
 1915 *Professor W. A. Haswell, M.A., D.Sc., F.R.S.
 1917 *Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
 1918 *Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
 1920 *Joseph Edmund Carne, F.G.S.
 1921 *Joseph James Fletcher, M.A., B.Sc.
 1922 *Richard Thomas Baker, The Crescent, Cheltenham.
 1923 *Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
 1924 *Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
 1925 *Charles Hedley, F.L.S.
 1927 Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
 1928 *Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
 1929 Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.
 1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.
 1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.
 1932 *Frederick Chapman, A.L.S., F.R.S.N.Z., F.G.S., Melbourne.
 1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.
 1934 *Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.
 1935 *George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.
 1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.
 1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.
 1938 *Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.
 1939 *C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.
 1941 Professor Frederic Wood Jones, M.B., B.S., D.Sc., F.R.S., Anatomy Department, University of Manchester, England.
 1942 William Rowan Browne, D.Sc., Reader in Geology, The University of Sydney, N.S.W.
 1943 Walter Lawry Waterhouse, M.C., D.Sc.Agric., D.I.C., F.L.S., Reader in Agriculture, University of Sydney.
 1944 Professor Wilfred Eade Agar, O.B.E., M.A., D.Sc., F.R.S., University of Melbourne, Carlton, Victoria.
 1945 Professor William Noel Benson, B.A., D.Sc., F.G.S., F.R.G.S., F.R.S.N.Z., F.G.S.Am., University of Otago, Dunedin, N.Z.
 1946 Black, J. M., A.L.S. (*honoris causa*), Adelaide, S.A.
 1947 *Hubert Lyman Clark, A.B. D.Sc., Ph.D., Hancock Foundation, U.S.C., Los Angeles, California.
 1948 Walkom, Arthur Bache, D.Sc., Director, Australian Museum, Sydney.
 1949 Rupp, Rev. H. Montague, 24 Kameruka-road, Northbridge.

AWARDS OF THE JAMES COOK MEDAL.

Bronze Medal.

Awarded annually for outstanding contributions to science and human welfare in and for the Southern Hemisphere.

- 1947 Smuts, Field-Marshal The Rt. Hon. J. C., P.C., C.H., K.C., D.T.D., LL.D., F.R.S., Chancellor, University of Capetown, South Africa.
 1948 Houssay, Bernardo A., Professor of Physiology, Instituto de Biología y Medicina Experimental, Buenos Aires, Argentina.
 1949 No award made.

AWARDS OF THE EDGEWORTH DAVID MEDAL.

Bronze Medal.

Awarded annually for Australian research workers under the age of thirty-five years, for work done mainly in Australia or its territories or contributing to the advancement of Australian Science.

- | | | | |
|------|--|---|--------------|
| 1948 | Giovannelli, R. G., M.Sc., Division of Physics, National Standards Laboratory, Sydney. | } | Joint Award. |
| | Ritchie, Ernest, M.Sc., University of Sydney, Sydney. | } | |
| 1949 | Kiely, Temple B., D.Sc.Agr., Caroline-street, East Gosford. | | |

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

- 1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."
- 1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal.

- 1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."
- 1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."
- 1887 Jonathan Seavor, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."
- 1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."
- 1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."
- 1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."
- 1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."
- 1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."
- 1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."
- 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
- 1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."
- 1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."
- 1943 Edwin Cheel, Sydney, in recognition of his contributions in the field of botanical research and to the advancement of science in general.
- 1948 Waterhouse, Walter L., M.S., D.Sc.Agr., D.I.C., F.L.S., Sydney, in recognition of his valuable contributions in the field of agricultural research.
- 1949 Elkin, Adolphus P., M.A., Ph.D., Sydney, in recognition of his valuable contributions to the field of Anthropological Science.

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £75.

Established as the result of a generous gift to the Society by Dr. W. F. BURFITT, B.A., M.B., Ch.M., B.Sc., of Sydney, which was augmented later by a gift from Mrs. W. F. BURFITT. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past six years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

- 1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.
- 1932 Charles Hallibey Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
- 1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

- 1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.
 1941 Frederick William Whitehouse, D.Sc., Ph.D., University of Queensland, Brisbane.
 1944 Hereward Leighton Kesteven, D.Sc., M.D., c/o Allied Works Council, Melbourne.
 1947 John Conrad Jaeger, M.A., D.Sc., University of Tasmania, Hobart.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (THIS JOURNAL, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

- 1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.
 1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.
 1940 G. J. Burrows, B.Sc., University of Sydney.
 1942 J. S. Anderson, B.Sc., Ph.D. (*Lond.*), A.R.C.S., D.I.C., University of Melbourne.
 1944 F. P. Bowden, Ph.D., Sc.D., University of Cambridge, Cambridge, England.
 1946 Briggs, L. H., D.Phil. (*Oxon.*), D.Sc. (*N.Z.*), F.N.Z.I.C., F.R.S.N.Z., Auckland University College, Auckland, N.Z.
 1948 Ian Lauder, M.Sc., Ph.D., University of Queensland, Brisbane.
-

Royal Society of New South Wales

REPORT OF THE COUNCIL FOR THE YEAR ENDING 31st MARCH, 1950.

PRESENTED AT THE ANNUAL GENERAL MEETING OF THE SOCIETY, 5TH APRIL, 1950

(RULE XXVI).

The membership of the Society at the end of the period under review stood at 361, an increase of seven. Twenty-nine new members were elected during the year. However, 13 members were lost by resignation, and three, who were in arrears with subscriptions, were removed from the register. Six members have been lost to the Society by death since 1st April, 1949 :

Henry Harvey Dare (1890).

Walter John Enright (1916).

Joseph Foreman (1879).

Robert Thomas McKay (1891).

Dansie Thomas Sawkins (1941).

Charles Josiah White (1909).

Professor Sir Howard Florey, M.B., B.S., B.Sc., M.A., Ph.D., F.R.S., and Professor F. M. Burnet, M.S., Ph.D., F.R.S., were elected to honorary membership of the Society at the annual meeting on 6th April, 1949.

During the year eight General Monthly Meetings were held, at which the average attendance was 39. Forty-four papers were accepted for reading and publication by the Society—an increase of five from the previous year.

It has been the policy of Council to favour a broadening of the scope of the General Meetings and to encourage members other than the authors of papers to play an active part. In pursuance of this policy a portion of the time at general meetings has been devoted to "Notes, Exhibits and Questions".

During the year the following questions have been answered :

4th May :

"Why do stars twinkle and planets not?", by Professor O. U. Vonwiller.

1st June :

"When a number is raised to the fifth power, why is the figure in the units place the same as in the original number?", by Dr. R. L. Aston.

7th December :

"How are earthquakes located at a distance?", by Rev. D. J. K. O'Connell.

On the 7th September, also, the following exhibit was discussed :

"Crystal of Synthetic Rutile", by Dr. D. P. Mellor.

At the meeting held on 2nd November, the President announced that the Council of the Society had felt that there was need to organise an activity which would give members and their friends a better chance to meet and talk with one another than was possible at the ordinary formal meetings, and he welcomed members and their friends to the *Conversazione*.

The evening was devoted to Exhibits and Films of Scientific Interest, and this arrangement had been made possible through the courtesy of the following :

Australian Museum,
Department of Agriculture,
Museum of Technology and Applied Science,
National Standards Laboratory.
Sydney Technical College,
University of Sydney :
Chemistry Department, and
Geology Department.

At the meeting held on 1st June the following addresses were given :

"Notes on a Recent Journey to Europe", by Professor O. U. Vonwiller.

"Visits to Observatories in Europe and America", by Rev. D. J. K. O'Connell.

As has become customary, one meeting was devoted to the commemoration of great scientists. This meeting was held on 7th September, and at it the following addresses were given :

"Goethe's Work and its Significance in the Twentieth Century", by Professor R. B. Farrell.

"Edward Jenner and Vaccination", by Professor E. Ford.

"Life and Works of Pierre-Simon de Laplace", by Mr. H. H. Thorne.

Lecturettes given during the year were as follows :

3rd August :

"The Response of Marsupials to Pathogens", by Dr. A. Bolliger.

"Wolf's Creek Meteorite Crater", by Mr. R. O. Chalmers.

Five Popular Science Lectures were delivered during the year and were appreciated by members of the Society and the public :

19th May : "The Study of Earthquakes", by Professor K. E. Bullen.

18th August : "Radio Astronomy", by Mr. J. G. Bolton.

15th September : "Sex Control in Animals", by Dr. C. W. Emmerls.

20th October : "The Australian and American Arnhem Land Expedition of 1948", by Mr. F. D. McCarthy.

17th November : "War Surgery through the Ages", by Dr. N. R. Wyndham.

The Annual Dinner of the Society was held at the Sydney University Union on 30th March, 1950. There were present 89 members and friends.

The Section of Geology, whose Chairman was Dr. G. D. Osborne, and Honorary Secretary Mr. N. C. Stevens, held five meetings during the year, at which the average attendance was 15 members and seven visitors. The activities were :

29th April : Address by Dr. G. D. Osborne and Mr. J. S. Proud, entitled "Occurrence and Probable Genesis of Asbestos at Wood's Reef, near Barraba, N.S.W."

20th May : Discussion on "The Geology and Mineral Resources of Tasmania", led by Dr. W. R. Browne. Mr. R. O. Chalmers showed exhibits from mining centres of western Tasmania.

16th September : Address by Dr. L. E. Koch entitled "On Pyrophyllite, its Mineralogy, Minerogeny and Economic Prospects in Australia". The address was accompanied by an exhibit of specimens.

21st October : Address by Mr. N. C. Stevens entitled "The Geology of the Canowindra District, N.S.W."

18th November : Notes and Exhibits by Miss F. Quodling, Mr. F. N. Hanlon, Mr. H. O. Fletcher, Mr. R. O. Chalmers, Dr. D. Carroll, Dr. L. E. Koch, Mr. T. G. Vallance, Mr. W. H. Williamson, Mr. N. C. Stevens and Dr. G. D. Osborne.

The Council of the Society held twelve ordinary meetings during the year, at which the average attendance was 13.

On Science House Management Committee the Society was represented by Messrs. H. O. Fletcher and F. R. Morrison, with substitute representatives Dr. R. L. Aston and Mr. H. H. Thorne.

On Science House Extension Committee the Society was represented by Drs. A. Bolliger and R. L. Aston.

The Clarke Memorial Lecture for 1949 was delivered by Dr. W. R. Browne on 16th June, the title being "Metallogenetic Epochs and Ore Regions in Australia".

The Clarke Memorial Medal for 1950 was awarded to Dr. Ian Murray Mackerras, Director, Queensland Institute of Medical Research, Brisbane, in recognition of his distinguished work on Diptera of the Australian region.

The Medal of the Royal Society of New South Wales for 1949 was awarded to Professor A. P. Elkin in recognition of his valuable contributions to the field of Anthropological Science.

The Edgeworth David Medal for 1949 was awarded to Dr. Temple Bayliss Kiely for his research work in Plant Pathology.

The James Cook Medal was not awarded for the year 1949.

During the year several scientists from overseas visited the Society's rooms and were entertained by the President and Council. Among these were :

Sir Geoffrey I. Taylor, M.C., F.R.S., Fellow of Trinity College, Cambridge, and Yarrow Research Professor of the Royal Society. (11th May, 1949.)

Professor H. S. W. Massey, F.R.S., Goldsmid Professor of Mathematics at University College, University of London. (26th September, 1949.)

Dr. G. M. Lees, M.C., D.F.C., of the Anglo-Iranian Oil Co. Ltd. Dr. Lee was accompanied by Dr. Davies. (9th December, 1949.)

During his visit to Sydney, Dr. Lees delivered a lecture entitled "The Oilfields in the Middle East". The lecture, which was given under the auspices of the Royal Society of New South Wales and the University of Sydney, was given on 9th December, 1949.

On 12th January, 1950, the Society arranged a public lecture by Professor Sidney Chapman, Sedleian Professor of Natural Philosophy at the University of Oxford. The subject was "Aurora".

The first Pollock Memorial Lecture, sponsored by the University of Sydney and the Royal Society of New South Wales, was delivered by Professor T. M. Cherry of the University of Melbourne, on 28th October, 1949. The subject of the lecture was "The Flow of Gases".

The financial position of the Society, as disclosed by the annual audit, is not a satisfactory one.

The greatest single increase in the Society's expenses has been that of printing. The cost of production of the Society's Journal has increased from £12 per 16 pages, 1940, to £2 per page in 1950, and is still increasing. This, together with a steady increase in the number of papers accepted for publication, has meant that the Journal is now by far the costliest item on the balance sheet. The Council is fully alive to the threat to the Society's finances implicit in these trends, and desires to place the position clearly before members. Council believes that any curtailment in the publication of meritorious papers purely on the grounds of cost would be a retrograde step.

The scientific standing of the Society is linked with the quality of the papers published in its Journal. On the other hand, consideration of present costs makes it imperative for the Editor to impress upon authors the need for the utmost conciseness in expression. Council has found it necessary on several occasions this year to return papers to authors with a request for abbreviation. However, there is a limit to the extent to which any subject matter can be abbreviated and still remain intelligible, and a major subject for the deliberation of the incoming Council will be concerned with ways and means of meeting the rising cost of publication.

The Society's share of the profits from Science House for the year was £400.

The grant from the Government of New South Wales of £400 has been received. The continued interest of the Government in the work of the Society is much appreciated.

Original Manuscripts, Maps, etc.—At its meeting held on 27th July, 1949, Council decided that manuscripts, maps, etc., be made available to authors six months after publication.

The Library.—The amount of £38 4s. 8d. has been spent on the purchase of periodicals and £57 11s. 6d. on binding.

Exchange of publications is maintained with 399 societies and institutions, an increase of 12 over the previous year.

The number of accessions entered in the catalogue during the year ended 28th February, 1950, was 3,060 parts of periodicals.

The number of books, periodicals, etc., borrowed by members, institutions and accredited readers was 346.

The Society sold a number of bound volumes of early editions of *The Sydney Morning Herald* to the Library Board of Queensland for the sum of £86 10s.

Among the institutions which made use of the library through the inter-library borrowing scheme were: Australian Paper Manufacturers, Bureau of Mineral Resources, Colonial Sugar Refining Co. Ltd., Commonwealth Observatory, C.S.I.R.O., National Standards Laboratory, Division of Fisheries, Division of Food Preservation, Division of Industrial Chemistry, Division of Tribophysics, Elliotts and Australian Drugs, Forestry Commission, Melbourne University, M.W.S. and D. Board, New England University College, N.S.W. Department of Agriculture, Division of Wood Technology, Plant Research Laboratory, Public Library, N.S.W., Public Library, South Australia, Standards Association of Australia, Sydney Hospital, Sydney Technical College, Sydney University, Taubman's Ltd., University of Western Australia, Zinc Corporation.

HARLEY WOOD,
President.

THE ROYAL SOCIETY OF NEW SOUTH WALES.
BALANCE SHEET AS AT 28th FEBRUARY, 1950.

LIABILITIES.

| 1949. | | | 1950. | | |
|----------------|--|-------|----------------|----------|-----------|
| £ | | | £ | s. | d. |
| 141 | Accrued Expenses | | 470 | 6 | 0 |
| 26 | Subscriptions Paid in Advance | | 33 | 1 | 6 |
| 90 | Life Members' Subscriptions — Amount carried forward | | 107 | 5 | 0 |
| | Trust and Monograph Capital Funds (detailed below)— | | | | |
| | Clarke Memorial | 1,957 | 1 | 1 | |
| | Walter Burfitt Prize | 1,090 | 12 | 5 | |
| | Liversidge Bequest | 733 | 5 | 3 | |
| 7,245 | Monograph Capital Fund | 3,620 | 3 | 4 | |
| | | | 7,401 | 2 | 1 |
| 26,082 | ACCUMULATED FUNDS | | 25,579 | 11 | 3 |
| | Contingent Liability—In connection with perpetual leases. | | | | |
| <u>£33,584</u> | | | <u>£33,591</u> | <u>5</u> | <u>10</u> |

ASSETS.

| 1949. | | | 1950. | | |
|----------------|---|-------|----------------|----------|-----------|
| £ | | | £ | s. | d. |
| 440 | Cash at Bank and in Hand | | 403 | 1 | 6 |
| | Investments — Commonwealth Bonds and Inscribed Stock, etc.—at Face Value— | | | | |
| | Held for— | | | | |
| | Clarke Memorial Fund | 1,800 | 0 | 0 | |
| | Walter Burfitt Prize Fund | 1,000 | 0 | 0 | |
| | Liversidge Bequest | 700 | 0 | 0 | |
| | Monograph Capital Fund | 3,000 | 0 | 0 | |
| | General Purposes | 4,660 | 0 | 0 | |
| 11,160 | | | 11,160 | 0 | 0 |
| 24 | Prepayment | | | | |
| | Debtors for Subscriptions | 57 | 17 | 0 | |
| — | Deduct Reserve for Bad Debts | 57 | 17 | 0 | |
| 14,746 | Science House—One-third Capital Cost | | 14,835 | 4 | 4 |
| 6,800 | Library—At Valuation | | 6,800 | 0 | 0 |
| 379 | Furniture—At Cost—less Depreciation | | 360 | 0 | 0 |
| 27 | Pictures—At Cost—less Depreciation | | 26 | 0 | 0 |
| 8 | Lantern—At Cost—less Depreciation | | 7 | 0 | 0 |
| <u>£33,584</u> | | | <u>£33,591</u> | <u>5</u> | <u>10</u> |

TRUST AND MONOGRAPH CAPITAL FUNDS.

| | Clarke Memorial. £ s. d. | Walter Burfitt Prize. £ s. d. | Liversidge Bequest. £ s. d. | Monograph Capital Fund. £ s. d. |
|-----------------------------------|--------------------------------|--|-----------------------------------|--|
| Capital at 28th February, 1949 .. | 1,800 0 0 | 1,000 0 0 | 700 0 0 | 3,000 0 0 |
| Revenue— | | | | |
| Balance at 28th February, 1949 | 160 4 7 | 55 17 5 | 7 10 3 | 520 18 4 |
| Interest for twelve months .. | 64 14 0 | 34 15 0 | 25 15 0 | 99 5 0 |
| | 224 18 7 | 90 12 5 | 33 5 3 | 620 3 4 |
| Deduct Expenditure | 67 17 6 | — | — | — |
| Balance at 28th February, 1950 .. | £157 1 1 | £90 12 5 | £33 5 3 | £620 3 4 |

ACCUMULATED FUNDS.

| | £ | s. | d. |
|--|---------|----|----|
| Balance at 28th February, 1949 | 26,081 | 18 | 2 |
| Add Decrease in reserve for bad debts | 27 | 8 | 0 |
| | £26,109 | 6 | 2 |
| Less— | | | |
| Deficit for twelve months (as shown by Income and Expenditure Account) | £436 | 3 | 7 |
| Amount written off <i>re</i> James Cook and Edgeworth David Medals.. | 71 | 10 | 4 |
| Bad Debts written off | 22 | 1 | 0 |
| | 529 | 14 | 11 |
| | £25,579 | 11 | 3 |

The above Balance Sheet has been prepared from the Books of Account, Accounts and Vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 28th February, 1950, as disclosed thereby. We have satisfied ourselves that the Society's Commonwealth Bonds and Inscribed Stock are properly held and registered.

HORLEY & HORLEY,
Public Accountants.

Prudential Building,
39 Martin Place,
Sydney, 20th March, 1950.

INCOME AND EXPENDITURE ACCOUNT.

1st March, 1949, to 28th February, 1950.

| 1948-9. | | 1949-50. | |
|---------|---|----------|-------|
| £ | | £ | s. d. |
| 640 | To Printing and Binding Journal—Vol. 82 | 1,001 | 19 0 |
| 468 | „ Salaries | 520 | 0 11 |
| 133 | „ Library—Purchases and Binding | 113 | 4 8 |
| 103 | „ Printing—General | 101 | 12 0 |
| 97 | „ Miscellaneous | 68 | 2 2 |
| 74 | „ Postage and Telegrams | 57 | 14 2 |
| 55 | „ Rent—Science House Management Committee .. | 54 | 1 11 |
| — | „ Entertainment Expenses | 16 | 8 11 |
| 37 | „ Cleaning | 36 | 0 0 |
| 23 | „ Depreciation | 21 | 4 0 |
| 22 | „ Telephone | 14 | 11 11 |
| 23 | „ Insurance | 23 | 13 5 |
| 19 | „ Audit | 18 | 18 0 |
| 9 | „ Electricity | 4 | 17 6 |
| 2 | „ Repairs | 12 | 18 6 |
| | „ Reprints— | | |
| | Expenditure £104 0 6 | | |
| | Less Received 81 1 3 | | |
| 56 | | 22 | 19 3 |
| | „ Annual Dinner— | | |
| | Expenditure £88 4 4 | | |
| | Less Received 69 14 9 | | |
| 39 | | 18 | 9 7 |
| 1,800 | | | |
| 228 | „ Surplus for Twelve Months | | |
| £2,028 | | | |

| 1948-9. | | 1949-50. | |
|--------------|---|--------------|-------|
| £ | | £ | s. d. |
| 586 | By Membership Subscriptions | 599 | 0 6 |
| 400 | „ Government Subsidy | 400 | 0 0 |
| 391 | „ Science House—Share of Surplus | 400 | 0 0 |
| 156 | „ Interest on General Investments | 161 | 13 2 |
| 478 | „ Proceeds Sale of Old Library Books | 89 | 17 8 |
| 5 | „ Other Receipts | 11 | 1 0 |
| 12 | „ Proportion of Life Members' Subscriptions | 9 | 0 0 |
| <hr/> 2,028 | | <hr/> 1,670 | 12 4 |
| — | „ Deficit for Twelve Months | 436 | 3 7 |
| <hr/> £2,028 | | <hr/> £2,106 | 15 11 |

Obituary

HENRY HARVEY DARE, a member of this Society since 1890, was born at Goulburn on August 25th, 1867, and died at Sydney on August 20th, 1949. He was educated at Sydney Grammar School and Sydney University, where he graduated as Bachelor of Engineering in 1888 and Master of Engineering in 1894, having been awarded a University Medal with each degree. After a short period on the staff of Sydney Observatory he entered, in 1895, the Public Works Department of New South Wales. He was responsible for the design of many public works. His last position with the Public Works Department was that of Chief Engineer for National Works and Drainage. When the Water Conservation and Irrigation Commission was constituted in 1913, he was appointed Chief Engineer to the Commission, and in 1915 Engineering Commissioner. He retired at the end of 1934.

The completion of Burrinjuck Dam, the construction of Wyangala Dam, works on the Murrumbidgee Irrigation Area and the establishment of Coomealla Irrigation Area, as well as the investigations of many of the proposals for water conservation throughout the State, were carried on under his direction. These have had a large influence on the development of Australian rural areas.

He was the New South Wales representative of the River Murray Commission from its inception in 1917 and a consultant on many major water supply works throughout Australia and New Zealand.

He was a member of a board appointed in 1918 to enquire into the extension of the water supply for Sydney, which recommended the construction of the Cordeau, Avon and Nepean Dams. The increase in average daily water consumption in Sydney from 41 million gallons in 1918 to 131 million gallons at present is sufficient to show the magnitude of the works in which he played an important part.

Mr. Dare was of retiring disposition and was held in high respect and esteem by all who knew him, especially by the staff who came under his control. He took an active part in the affairs of the professional bodies to which he belonged, and was a member of the Council of The Institution of Engineers of Australia, which awarded him the Peter Nicol Russell Medal. His death terminates the career of one of Australia's outstanding civil engineers.

WALTER JOHN ENRIGHT, who died on September 27th, 1949, was born on March 10th, 1874, at West Maitland, N.S.W. After two years in his father's auctioneering business he entered the legal profession, and graduated B.A. in 1893. It was while pursuing his University studies that he came under the influence of Professor David, being in one of the latter's first geology classes in the early nineties. The impress of Professor David on Enright's life was indelible, and although he was a very successful lawyer, becoming known throughout the Hunter River Valley, he never lost his love for geology, and indeed for many branches of natural history.

He was an amateur scientist of distinctly high calibre. His observations in various fields of natural science were accepted by professional scientists, and he was constantly appealed to by those seeking information about local geology, entomology, forestry, ichthyology and anthropology.

He wrote several useful original articles on some of these branches of science, and was instrumental in promoting research in many areas by assisting the work of the pioneers in various parts of the State, but particularly in the Hunter-Manning regions. His great energy, wide knowledge, tact and public spirit led to his assuming a leading place in his community, and he was actively associated with many worthy causes, especially with scientific and educational conferences or expeditions that were arranged in the northern part of the State. He played a dominant rôle in the whole organization of the visit to the Maitland district of Section C of the British Association in 1914.

He travelled widely in Australia and in the South-west Pacific, and his journeyings were always fruitful in scientific observations and in collection of exhibits.

Walter Enright will perhaps be best remembered by a host of friends of all classes because of his unflinching generosity and characteristic readiness to offer his services for any purpose to facilitate the work and promote the happiness of others.

He was elected a member of this Society in 1916.

ROBERT THOMAS MCKAY was born on December 31st, 1865, and died August 10th, 1949. He had a distinguished career as a civil engineer and administrator of engineering projects. After a period of training he qualified under the Mining Act of New South Wales and was appointed surveyor of the Engineering Branch of the Department of Public Works, New South Wales. From 1896 to 1902 he was Resident Engineer of the Sydney and Suburbs Sewerage Scheme

and he was responsible for a number of important works carried out during his term of office. He was principal officer of the Interstate Royal Commission on the Murray River (1902-1903) to enquire into the allotment of waters as between New South Wales, Victoria and South Australia for the purposes of water conservation, irrigation and navigation, and the report of this Commission has served as a basis for the many negotiations which have taken place since on this important problem. His expert knowledge in this matter was recognized by an invitation to address a Premier's Conference. He made a special study of riparian rights, the control of water by the Crown and the supply and distribution of artesian water.

From 1905 till 1911 he was Engineer and Executive Member of Water Conservation, Irrigation and Drainage Board, and was associated with many irrigation projects throughout the State, particularly on the Murray, Lachlan and Murrumbidgee Irrigation schemes. He was subsequently Chief Assistant Hydraulic Engineer for the State of Queensland and later Chief Engineer for the Geelong Water Works and Sewerage Trust and Engineer for Wheat Storage in connection with the bulk handling of wheat. His final important public post was that of Engineering Member and Deputy President of the Sydney Harbour Trust from 1922 to 1930.

He was an advocate for using the waters of the Snowy River to supplement the flow of the Murrumbidgee and to provide a supply to Sydney. He was one of the earliest pupils of Sydney High School and throughout his life took a great interest in the school, being very active in assisting its advancement, particularly at the time when its new buildings were erected at Moore Park. After his retirement from the Sydney Harbour Trust he undertook private practice as a consulting engineer. He was a member of the Council of the Advisory Committee of the Institution of Civil Engineers for many years and occupied the position of Chairman of the Council for six years.

He had been a member of the Royal Society of New South Wales since 1891.

JOSEPH FOREMAN was born on August 23rd, 1852, at Pemberton, near Wigan, in Lancashire, England, and was trained in his father's profession of medicine at Edinburgh and at London, qualifying as a surgeon at Guy's Hospital in 1873.

He then became Medical Officer on S.S. *Bonny*, conveying troops to Sierra Leone to the Ashanti War, and in the following year was appointed Medical Superintendent on the ship *Baron Aberdare*, taking some hundreds of immigrants to Auckland, New Zealand.

He stayed in New Zealand as Medical Officer at Waimate, in the Bay of Islands, from August, 1875, until 1877, when he came to New South Wales, and for the next two years he practised in the Richmond River district.

In 1879 he set up in practice in Sydney and became interested in various medical, cultural and industrial societies, including this Society.

He was appointed Surgeon on the Medical Staff of the N.S.W. Volunteer Forces in 1881. Later in the same year he visited Europe, where he studied under the famous Berlin surgeon, Augustus Martin, and also obtained further experience at the London Hospital for Women.

On his return he became Sydney's first specialist in obstetrics and gynaecology and was appointed Honorary Surgeon at the Royal Prince Alfred Hospital, retaining his association with that institution until his death. He was also on the Honorary Staff of the Royal Hospital for Women, and Lecturer on Diseases of Women in the University of Sydney until 1920. Students who attended his lectures recall his precise, calm and dignified manner and his stress on meticulous cleanliness, tidiness and punctuality.

Besides achieving eminence in his chosen profession, he had an interest in farming and on his retirement from active medical practice, when over 70 years of age, he invested in pastoral properties at Cooma, Condobolin and Meadow Flat, near Bathurst. In 1948 the proceeds of the sale of some of these properties (£20,000) were devoted to the foundation of fellowships in connection with Royal Prince Alfred Hospital.

At the time of his death on January 15th, 1950, Dr. Foreman was the oldest member of this Society, having been elected in 1879.

CHARLES JOSIAH WHITE, a member of this Society since 1909, was born in 1881 at Wollongong, N.S.W., and received his early education at Wollongong.

He began his life-work in the teaching profession as a pupil-teacher at Gerringong and later at Wollongong. In 1902 he entered the Teachers' Training College at Fort Street Model School. After a distinguished undergraduate career in the University of Sydney, he graduated Bachelor of Science in 1907 with the University Medal for Chemistry, of which he was the first recipient, and Bachelor of Arts in 1908.

On the completion of his University course he was appointed Lecturer-in-Charge of Science at the Teachers' Training College, Sydney, and in this position he exercised a great influence on the teaching of science in the secondary schools of New South Wales until his retirement in 1945.

He died on July 31st, 1949.

DANSIE THOMAS SAWKINS, a member of this Society since 1941, was born on August 1st, 1880, at Muswellbrook, N.S.W., and died on March 22nd, 1950.

After his early education at Maitland he graduated from Sydney University as Bachelor of Arts with the University Medal for Mathematics in 1899, and Master of Arts in 1902. As James King of Irrawang Travelling Scholar he went to Cambridge, England, and graduated a Wrangler in 1904.

From 1904 to 1907 he was a schoolmaster in England; he then went to Siam and the Federated Malay States as a surveyor for five years, and on his return to New South Wales he worked as a surveyor in the State service for about five years.

Between 1917 and 1938 he was Statist to the Board of Trade and the Industrial Commission. He became Lecturer in Statistics at the University of Sydney in 1922 and in 1924 was appointed Peter Nicol Russell Lecturer in Geodesy. In 1938 he joined the full-time staff of the University of Sydney as Reader in Statistics.

He published a large number of papers on various aspects of statistics both in Australia and abroad, three of which appear in the *Journal and Proceedings* of this Society.

PRESIDENTIAL ADDRESS

By HARLEY WOOD, M.Sc.

Delivered before the Royal Society of New South Wales, April 5, 1950.

THE WORK OF THE SOCIETY.

The Annual Report of our Society indicates a year of useful activity. The usual monthly meetings were held, except for the one in July, which was cancelled owing to power restrictions. In August an afternoon meeting was held in the Geology Lecture Theatre at the University. The meetings of May, June, October and December were devoted mainly to the presentation of original papers and to lecturettes in the form of answers to questions brought forward by members. At the August meeting we had two lectures by members of the Council; the September meeting commemorated the centenaries of Goethe, Jenner and Laplace, and the November meeting took the form of a conversazione, at which there were films and exhibits of scientific interest. Sitting, as I have done as your President, on the dais in front of the meeting, I have not been able to avoid noticing that the number of members who attend varies as the amount of material of general interest on our agenda. When we have devoted our attention entirely to the presentation and discussion of original papers, the audience has been just comfortably over the number we need for a quorum, whereas at the September and, especially, the November meetings our hall was well filled. In this respect the introduction into our meetings of questions by members has certainly proved a satisfactory way of finding interesting topics and speakers who might not otherwise have come forward. Naturally, many authors who present papers to the Society are anxious to have them discussed at a meeting, but, in view of experience while I have been in the chair, and indeed, observation for some years past, I believe that all such presentations should be as nearly popular as possible. In most cases our audience can only have a very few specialists in the subject of a paper, and it is necessary for authors to speak more at the level of the unsophisticated majority. It should usually be possible to explain the background of a piece of research in such a way that most of us can understand the kind of contribution which is being made.

The Clarke Memorial Lecture for 1949 was delivered by Dr. W. R. Browne, who spoke on "Metallogenetic Epochs and Ore Regions in Australia". During the year there were five popular science lectures. All of these produced satisfactory audiences and, in three cases, the hall was full to overflowing.

Two years ago the Council of the Society decided to institute a series of monographs, and this year the first one to be accepted was presented by Dr. G. D. Osborne. It is entitled "The Structural Evolution of the Hunter-Manning-Myllal Province".

It is my pleasant duty to thank the members of the Council, and indeed the general membership of the Society, for the cooperation I have received during the year and for their goodwill, which has made it a pleasure to preside at our meetings. My thanks are due especially to the Honorary Executives who have carried on the work with such devotion. Dr. Bosworth has kept able hands on the management of the Society's affairs. Mr. Smith-White, as editor, Dr. Bolliger as treasurer and Mr. Hanlon as librarian have given without stint time, energy, and in each case more than ordinary skill.

We live in an age when man is bewildered by his own technical achievement. Science has placed in his hands a power altogether beyond the dreams of our forefathers—a power that may be used for good or for destruction. The atomic physicist has already demonstrated the destructiveness of his contribution, but has only just begun to tame his monster so that it may be used for the service of society. The biological scientist, not to be outdone, insists that he has weapons available which can strike a blow no less terrible than the atomic bomb.

The questions posed by the enhanced possibilities for purposive destruction, important as they are, represent only a part of the problem that is being thrust on mankind. We have seen more clearly than ever before that, in a few generations, man can use up the resources of power which nature in past ages has gathered from the sun and stored beneath our soil. We know that a few generations of misuse can so reduce the fertility of that soil that the precarious existence we now wring from it, and we must not forget that for the bulk of mankind it is precarious, will be endangered.

The suggestion is often made that certain weapons of war should be outlawed; but war is the negation of law and it is not conceivable that a nation would allow itself to be defeated, leaving unused a weapon which might bring victory. According to recent press reports, Einstein has stated his belief, and I think he is right, that the real alternative is that the political leaders of the world will be deterred from war for a period long enough for the world to evolve some sort of central government. In the past, the tendency has been for larger groups of mankind to be formed by the amalgamation of smaller ones. One group might conquer its neighbour, or combine with it through the fear of a third power, and throughout history the powerful interest that has compelled loyalty of different groups to common leaders, has been the threat of some external aggressor. Now that the enemy is recognized to be war itself, surely we can feel and foster a loyalty to mankind as a whole.

Science now has prestige, responsibilities and, especially, dangers that it had not before. The characteristic of science is that every hypothesis should undergo the searching test of discussion and comparison with observation, and we have come to realize that, even such larger advances as the invention of the quantum theory are only scaffoldings on which to unify the knowledge already gained before proceeding to build further. Science distinguishes real advances, which provide tests to which observation can be directed and to which they stand up, from those which cannot be applied in a way which will test their truth, and it implies a complete freedom of thought and of criticism, and the display for criticism of all ideas within the realm of human knowledge. It is by such means that knowledge advances. Now the advancement of knowledge and the greater dissemination of it are essential if humanity is to be freed from the chains placed upon it by want and fear. We all know that the power over nature he now wields has produced a tendency to place restrictions on the scientist and on free interplay of scientific discussion and criticism. This applies in almost all countries of the world at present, and most members will be able to recall cases of men of science having their activities restrained in some way or other. Well publicized examples of interference with the freedom of science have occurred in many countries. A characteristic of this age is its science and technology, and one phase of this is that many of the most alert and able minds of the time are being attracted to science. One can observe signs that, if science were to lose that freedom in which such alertness can flourish, it would begin to wither for want of support. It has been freely stated that, despite advantages offered in the way of opportunity for research and in the way of equipment of the very best kind, the best scientists are not attracted to government laboratories dealing with the development of weapons of war; and if the attitude

of the community becomes further unfavourable to the work of science there will be little attractiveness left in it.

In such a background our Society has an opportunity and a duty to provide a forum for the discussion among scientists of matters of general interest which affect them in their professional work. An example of this sort of discussion was the symposium on "The Education of a Scientist", which we held in 1948 and which aroused considerable interest, but I believe that we should occasionally have discussions on more controversial, and probably more vital, matters. On the other hand we need to foster the penetration of the scientific outlook into our Australian community and, while we now do this in some degree by our popular science lectures, it will be readily admitted that there is a great need for work which is more explicitly directed towards improving the prestige of science.

Wherever I have been as your representative I have found our Society held in high esteem. It is the only society in New South Wales which unites all of the sciences; other organizations are limited to one science or group of sciences or by being professional associations, whose proper care is for the status of their members.

Of the various organizations to which I have belonged this is the one of whose usefulness I feel most convinced and the association with which affords me most satisfaction.

We must continue our work despite the difficulty of the times, indeed, in some respects, because of it. We must endeavour more consciously, on the one hand, to foster public interest in science and to make known the value of science and scientific research in the economy and in the culture of our country and, on the other hand, to provide more and more a meeting-ground for the various specialist sciences and for the scientists who practise them.

ASTRONOMY IN AUSTRALIA.

THE HISTORY OF ASTRONOMY IN AUSTRALIA.

Astronomy was closely associated with the beginning of British settlement in Australia. The idea of using the observation of a transit of Venus to determine the distance of the Sun was first suggested by Kepler, and again with more practical detail by Halley in his report of the observation of a transit of Mercury, which he saw at St. Helena in 1677 and published with his Catalogue of Southern Stars. It was important that this constant, the fundamental unit of the Solar System, should be determined with all practicable accuracy and the scientific world was anxious to make use of the transits of Venus in the eighteenth century, sending on each occasion expeditions to distant parts of the world. For this reason James Cook was despatched to Tahiti to make observations there. The transit was observed on April 13, 1769, and the published results (Green and Cook, 1771) although not as precise as had been hoped, because of unexpected observational difficulties, nevertheless did yield an improved value of the solar parallax.

On this scientific expedition Cook made the exploration of the east coast of Australia which led to the foundation of the colony in 1788. With Captain Phillips' first fleet, too, there was an astronomer, Second Lieutenant William Dawes. One of his duties was to establish a post from which he was to attempt to observe the expected return of a comet.

Among the comets which had been discussed by Halley were two observed in 1532 by Appian and in 1661 by Hevelius. Having calculated that they had similar orbits, Halley conjectured that they were identical and that a new return would occur about 1790. This was discussed by Maskelyne (1786). The anxiety to observe this object was quite natural because at this stage the only

predicted return of a comet which had been verified was the famous one of Halley, and the only other body added by observation to the classical members of the Solar System was the planet Uranus. Several writers who refer to this matter mention that Dawes made no observation of this comet, and indeed, that no purely scientific observations were known to be produced from his observatory. They do not appear to add, however, that this is quite natural, since the comet was also not observed in the northern hemisphere where it should have been seen to better advantage, although at a later stage. In any case, Halley's conjecture was probably wrong, as the observations of the earlier comet are from the viewpoint of orbit computation not satisfactory, and computations differ a good deal as to the real character of the orbit of the comet of 1532. Dawes, too, could scarcely have been expected to undertake other astronomical work since, as well as being charged with the care of a small garrison, he was a very active member in the survey and exploration of the young colony. Besides other maps prepared later, he made a sketch of an area of the southern shore of Sydney Harbour as early as July 1788, on which his observatory is marked, its position being noted as longitude $151^{\circ} 19' 30''$ and latitude $-33^{\circ} 52' 30''$.

When Sir Thomas Brisbane was appointed Governor of New South Wales the British Government had already decided to establish an observatory at the Cape of Good Hope and so there was no opportunity for him to persuade his government to establish with public funds another observatory in the southern hemisphere. He determined himself to erect an observatory near to Government House in Parramatta. He arrived in Sydney in November 1821, and his instruments were set up in time to observe the solstice in December. His interest in the scientific culture of New South Wales is shown by the fact that before the end of 1821 he became president of the newly formed Philosophical Society of Australia, which was the predecessor of the Royal Society of New South Wales. The success of the work at Parramatta is shown by the fact that the three workers in the Parramatta Observatory, Brisbane himself, Dunlop and Rumker, all received the Gold Medal of the Royal Astronomical Society. One important piece of work done at Parramatta Observatory was the observation of Encke's Comet on its first predicted return in 1822. This was only the second case of a predicted return of a comet being verified, although several other comets had periodic orbits attributed to them by this time. After Brisbane's departure Parramatta Observatory was carried on, first by Rumker and then by Dunlop, but was finally closed in 1847.

Sir William Denison became Governor General in 1855, having previously been Governor of Van Diemen's Land, and it was due to his representation that the present Observatory was established. William Scott was appointed on the recommendation of the Astronomer Royal and arrived in Sydney in November 1856. The present building was started in 1857 and observations commenced in June 1858. Scott was honorary secretary of the Royal Society of New South Wales from 1867 to 1874 and honorary treasurer for several years. He joined in 1856 when it had newly assumed the title "Philosophical Society of New South Wales", and was the oldest member of the Society before he died in 1917. Indeed, astronomy in New South Wales has always been closely associated with our Society, and besides the influence of Brisbane it may be mentioned that of the six directors of the Observatory five have held executive positions in the Society and four have been president or held office equivalent to the presidential status.

As its share of an international plan to catalogue the positions of stars to a faint magnitude over the whole sky, Sydney Observatory undertook responsibility for the zone between south declinations 51° and 65° . In recent years most of the work of the Observatory has been associated with this Astrographic Catalogue,

somewhat more than half of which is now published and in the preparation of which several meridian catalogues have been prepared. Sydney Observatory has also published work on double stars and occultations of stars by the Moon.

Williamstown Observatory was founded in 1853 when R. L. J. Ellery was appointed by the Government of Victoria but it was dismantled in 1863 and the instruments were moved to Melbourne. Among the instruments Melbourne Observatory acquired was an 8" meridian circle installed in 1884 and the 48" reflector installed in 1869. Melbourne Observatory was closed as a State institution by the Victorian Government in 1944. Several valuable catalogues of star places based on meridian observations were left and are being prepared for publication by the Commonwealth Observatory. It may be possible to make arrangements to complete at Sydney Observatory the Melbourne section of the Astrographic Catalogue from -64° to the South Pole. As comment on the closure of Melbourne Observatory, I would say that it has since been necessary to provide telescopic demonstrations for educational purposes and to carry on certain other services of the old Observatory, and so the financial saving made by the decision to close the Observatory by no means equals the whole of the expenditure which was formerly made on it.

In 1855 Charles (later Sir Charles) Todd was appointed Superintendent of Telegraphs and Astronomical Observer for the colony of South Australia; and in 1874 the Adelaide Observatory was erected and provided with instruments. It has issued a series of publications on Jupiter, carried on some meridian observations and maintained observations of variation of latitude, which are part of an international cooperative plan. Most of the Adelaide Observatory buildings have now been demolished to make room for a school and it is intended to make the University responsible for future astronomical work.

Perth Observatory was founded in 1896 when W. E. Cooke was appointed Government Astronomer for Western Australia. In 1900 Perth undertook a share of the Astrographic Catalogue between -31° and -41° and its published work consists of meridian catalogues associated with reference stars for this work, and various volumes of the Catalogue, most of which has been published.

Although we are discussing chiefly professional astronomy, no account of the subject in Australia would be complete without mention of John Tebbutt, who worked as an amateur from about 1854 until 1904, maintaining at Windsor an observatory which became known throughout the world. He made altogether over 350 contributions to scientific journals, largely observations of comets, minor planets and double stars. Astronomy has had many celebrated amateurs. If we exclude those who became and worked much as professionals, John Tebbutt would rank very high indeed among the contributors to astronomical science.

Two further astronomical observatories have been established in Australia in this century. Riverview College Observatory was established by the Society of Jesus as a seismological station in 1908, with Father E. F. Pigot as first director, and in 1931 began astronomical observations. Valuable contributions are being made to astronomy by this Observatory, particularly important being the study of variable stars of the southern skies.

After careful testing of conditions on Mt. Stromlo, a few miles west of the Australian capital at Canberra, it was decided to establish an observatory there and a staff was appointed which began work in Canberra in 1925 and observations on Mt. Stromlo in 1926. Thus was established the strongest astronomical institution that Australia has had. It was called the Commonwealth Solar Observatory, but has now been renamed the Commonwealth Observatory to correspond more with its wider purpose. In its comparatively short life it has become an important contributor to research in a widening field of astronomical endeavour. The 48" telescope, formerly at Melbourne, is being modernized at Mt. Stromlo and soon a 74" reflector will be working beside it.

ASTRONOMY AS AN OPPORTUNITY TO AUSTRALIAN SCIENCE.

For any country there are always subjects of research which represent a special obligation or, in some cases, a special opportunity. Thus unless we in Australia investigate the meteorology of our country and its natural resources, we will leave a gap in information which is important, not only for ourselves, but as part of a world picture. A president of our Society, in his address four years ago, pointed out that we are under an obligation to study Australia's marsupial fauna. For Australians there is a similar obligation to astronomy. The object of my address is to point this out and at the same time to show that northern astronomers planning work in the southern hemisphere should consider coming to Australia. Because the great bulk of the wealth and population of the world must always remain in the northern hemisphere and, because there are important parts of the heavens not visible from the latitudes of Europe, North America or Asia the countries of the southern hemisphere can make a contribution to astronomical science more than proportional to the resources used, when compared to the efforts of northern astronomers. The study of the structure of the star-system in which our Sun is situated, or of the organization of the systems of which ours is but one, is impeded if the knowledge of a large area of the sky is comparatively incomplete. There is ample evidence of the need for astronomical research in the southern hemisphere to be brought in line with that of the north, and of the great opportunities which exist this side of the equator in the fact that observatories of many northern countries have expensive branch observatories in southern foreign lands. By far the greatest power of equipment is in the northern hemisphere. Of reflecting telescopes equal to or exceeding 36" in aperture, there are 27 in the world, of which four are in the southern hemisphere and only one in Australia. Of the refractors 24" or more in aperture, there are 26 in the world, six in the southern hemisphere and none in Australia.

To indicate the ways in which Australia can contribute towards astronomical research, let us first list the objects of study towards the understanding of which research is directed. These are :

1. The structure of the Solar System ;
2. The physical constitution of members of the Solar System ;
3. The physics of the Sun, which, of course, might be included as a member of the Solar System or as a particular star, though the study of the Sun is so important that it deserves a heading of its own ;
4. The structure of the Galaxy and of other star systems ;
5. The physical constitution of individual objects in the Galaxy including, for example, stars and the gaseous nebulae ;
6. The structure of the Universe.

Until the end of last century the emphasis in effort was mostly on the first two of these subjects ; but in this century the fourth and fifth have become of dominant importance, and it is likely that as time goes on the last one will advance beyond the pioneering stage and assume a greater place in the thoughts of the working astronomer. In the year books of the Carnegie Institution of Washington of almost fifty years ago concern was expressed at the lack of data on the southern skies as compared to those of the north, and ways of improving the situation were discussed. It was pointed out that the positions and proper motions of southern stars were required to facilitate the study of the motion of the Sun and the then newly discovered streaming of stars. (We now recognize other important systematic motions requiring study.) The important positional work done by the expedition to San Luis, the work of the Cape Observatory over a long period and the zone catalogues of the La Plata Observatory have improved this position very greatly and the data in the General Catalogue is not

yet fully discussed. However, it is necessary still to remember that observations must go on and that the resources of positional astronomy in the south remain below those of the northern hemisphere. At Sydney Observatory we are planning to continue positional work. By re-photography of the astrographic zones and comparison of the new plates with old ones, reliable proper motions should be obtainable; we will be mounting a new specially designed photographic lens on the astrographic telescope. The pioneering stage is now over and only observations of the highest quality will make a useful contribution. Fifty years ago it was also pointed out that the southern hemisphere was seriously behind in observations of stellar parallax and of double stars, and in capacity to make such observations. This position has been largely improved by the work of the Cape Observatory, the Bosscha Observatory at Lembang, the Yale University Observatory station at Johannesburg, the Union Observatory, Johannesburg, and the Lamont-Hussey Observatory of the University of Michigan. It was remarked, too, that the knowledge of radial velocities of the southern objects was falling behind the knowledge of those of the northern hemisphere, and that photometry of the stars of the southern sky was very much needed; and these deficiencies remain.

Among the most fundamental of the data required to study the galactic system are well determined magnitudes for the stars concerned. Careful observations have been made for a long time; for example, William and John Herschell made determinations more than 100 years ago and so we would expect there to be a great body of reliable data; but actually our knowledge of stellar magnitudes is much below the needs of astronomy and there is much work to be done in the northern hemisphere and the south is still very far behind. It is hard to imagine observational astronomy in a condition where there will not be a need for a substantial amount of photometric work on the stars. The apparently slow progress made in developing reliable stellar photometry is due to the difficulty of the observations which have to be made, and only gradually have the number and complexity of the systematic errors revealed themselves. At first, the photometry was done visually and astronomers relied upon the eye to integrate the visible light of the stars in making comparisons of brightness between them. A similar principle was used when photographic magnitudes became common, but the stars, being of different temperatures and having their energy distributed through their spectra in different ways, are affected differently by the atmosphere, by the instrument, by the method of observing, or the personality of the observer, and so gradually it became necessary to evolve a more precise definition of magnitude which did not involve the allowance for so many variables. In recent years, the emphasis has come to be on monochromatic photometry, where only a narrow range of the spectrum of the star is used and where we can rely upon the atmosphere and the instrument affecting the light in a similar way for different stars. This gradual improvement in photometric method means that for modern needs much of the work has to be revised; indeed, in the southern hemisphere it has to be revised almost from the beginning. Work of this kind has been undertaken in observatories in South Africa and our own Commonwealth Observatory. There will be need for the magnitude-system to be extended to faint magnitudes, for the number of stars per square degree to various magnitude limits to be determined so that statistical methods may be applied to them in order to study the structure of the galaxy. The discovery and examination of transparent areas of the Milky Way is expected to yield important clues concerning its structure. By methods such as the study of the continuous spectrum of the stars at Greenwich, or as monochromatic photometry at different wave lengths at Mt. Wilson, the colours of the stars in the southern sky need to be studied to extend the work which has been done in the northern hemisphere. It will soon be necessary to follow

the northern workers into the infra-red region and it seems that the examination of continuous spectra of variable stars (particularly eclipsing ones) might yield some results of interest. This kind of work is valuable not only in studying the stars themselves but also in studying the inter-stellar material through which the light from the stars has to pass before it reaches us. Some of the light is absorbed by the material and the way in which it affects the colours of the stars has already taught us much about the distribution, density and nature of this material ; mostly, however, in northern hemisphere areas. Exploratory work on the spectrum lines arising from inter-stellar absorption is also much needed.

When we go beyond the galaxy there is need to find the total magnitudes of nebulae in the southern hemisphere which are beyond the reach of the northern observers, and to determine isophotal lines and make detailed spectral and photometric examination of resolved objects, particularly variable stars. In this connection it should be remembered that the Magellanic Clouds are the nearest of the star systems which can be surveyed as a whole from the outside and the study of them by all the methods which may be available should yield results of importance, not only in studying these systems but also, more fundamentally, in increasing our knowledge of the way in which the star systems behave. Statistical data on their stars, having regard to magnitude, spectral class and position in the system, are needed together with values of stellar motions, based upon radial velocity measures, and possibly on proper motion measurements ; for, if stars of the Magellanic Clouds have high systematic motions, it might be possible for them to be measured, although, if the motions are not substantial they will be very difficult to disentangle from the systematic motions of reference objects among the stars of our own galaxy. In addition to the important and widely interesting topics I have already mentioned, it should be remembered that many other problems need to be studied over the whole sky and require observation from both hemispheres. For example, research on meteors is more advanced in the northern hemisphere than in the south in spite of the valuable work of an amateur group in the Royal Astronomical Society of New Zealand. Most of the work of observing minor planets can be done from the northern hemisphere but there is still a need for cooperation from southern observers in observing minor planets which culminate well south of the equator at opposition or when the effects of parallax have to be examined or eliminated. The new lens at Sydney will be suitable for this kind of observation.

So far the most important deficiencies in apparatus in the southern hemisphere have been in the direction of large astrophysical equipment. This will be partly offset now that the Radcliffe telescope of Oxford University has been put into commission in South Africa and the 74" telescope at Mount Stromlo will be due in a few years.

Recently, the National Geographic Society (of America) and the California Institute of Technology have sponsored a project for mapping the whole of the accessible area of the heavens with the 48-inch Schmidt camera of Mount Palomar. Each section of the sky will be photographed once in red light and once in blue light. This will provide a survey which should uncover many interesting objects for detailed examination by the great reflectors and give important material for statistical work. There have been no Schmidt cameras in the southern hemisphere but this will be partly remedied now that the instrument operated by Harvard, Dunsink and Armagh Observatories is becoming available. Mount Stromlo, too, may adapt the 48" telescope to carry a Schmidt camera. As at least one of these is to be fitted with an objective prism another southern hemisphere deficiency will have been mitigated. There is no telescope corresponding to the 20" astrographic telescope at the Lick Observatory in the southern hemisphere ; nor, as far as I know, is there one projected. One of the purposes of this instrument was to refer the system of

stellar motions to the galaxies beyond our own and, unless the data becomes available for the southern part of the sky, this investigation might easily strike difficulties when the interpretation of the results is to be made.

One thing that must be remembered is that, although there are some men like Eddington and Russell whose powerful ideas enable them to contribute greatly to their science, nevertheless most of the important contributions to astronomy, such as the resolution of the nearer nebulae into stars earlier in this century, come from workers with powerful equipment and the most valuable contribution that southern workers can make is by observation. We must therefore see that our observatories have adequate and up-to-date equipment.

ON THE CHOICE OF SITES FOR OBSERVATORIES.

Having established that opportunity is good for astronomical work in the southern hemisphere, we need to decide whether there are suitable places for it in Australia. Let us list the requirements.

1. The site should be satisfactory from the meteorological point of view, having a good proportion of clear sky, a low average wind velocity, and a low average daily temperature range. Strong winds tend to cause instruments to vibrate and lead to lack of homogeneity of the atmosphere from an optical point of view, and a large temperature-range causes expansion and contraction of instruments, which is particularly undesirable in large optical parts.

2. A site some miles away from big industrial plant, or from a situation where such plant could come, is preferable ; for example, a large deposit of iron or coal might prove a bad neighbour.

3. Adequate supplies of electricity and water and accessibility by road or rail transport would be necessary, since, if they were not available, provision of them would take too much of the resources of all but the most ambitious schemes.

4. Living conditions for staff should be good and this implies reasonable proximity to town and educational facilities ; this is now recognized as desirable, even if only scientific efficiency is taken into account.

5. The atmosphere at the site should have a standard of transparency which is high and constant relative to varying position in the sky or to time. This is necessary for almost any work, and particularly for photometry. The background sky brightness should be low for photography with fast instruments. The meteorological corona must be low for some work.

6. For work requiring good image quality, such as measuring double stars or examining planetary detail, the seeing conditions require to be of high average quality.

These are very stringent requirements and much trouble is often taken to discriminate between available sites. Of course, a lot of the work can be done at the desk by examining meteorological and other statistical records, but it is necessary, in particular cases, to make quantitative estimates in the field of quality of the atmosphere before establishing a large and expensive institution. Sometimes, of course, considerations other than purely scientific suitability have to be taken into account. An observatory associated with a university should be near enough to the university for students to do observational work without the handicap of too much travelling.

It is also desirable that the site should be at least some distance from the sea, since, according to Middleton (1941) sea salt nuclei, even in smaller numbers, are more effective in limiting visual range than dust or combustion nuclei. Moreover in eastern Australia the coastal areas are inferior from the point of view of freedom from cloud. Regarding seeing conditions, it seems established

that there can be deficiencies which are very localized, as well as wide regional characteristics, and it would be indeed unwise to establish an observatory at a place where the topography showed marked lack of symmetry, as by the sea shore or on the slopes of mountains. In such places frequent diurnal winds are likely to be destructive of good seeing. Places at which there is a strong frequency of wind coming from higher topography should also be avoided, unless they have been tested. The bad effect this has on seeing conditions has been noted at many places.

It is always considered desirable to situate observatories at a considerable height above sea level in order to have below the observer a good deal of the atmosphere, including the part which, being least transparent and most subject to turbulence, interferes most with good optical quality of the air. The actual site should be somewhat above the surrounding landscape, in order to lift it above the ground haze, and above any dust which might be raised with particles large enough to fall quickly in the air. Elevation above the surrounding landscape also reduces the diurnal range of temperature. Another advantage is that the air should tend to settle downwards on the top of a hill at night. This should bring the haze level down at night and the gradual settling of the air should be favourable to good seeing conditions. In regard to atmospheric pollution from towns: it is well to remember that the effect is carried a good many miles to the lee of its source, and situations, whose prevailing winds might carry such pollution towards them must be regarded as unfavourable. The situation of the observing site above the surrounding topography will be of value towards eliminating this effect. However, when selecting a site for daytime observation, it might be preferable to avoid a hilltop about which air might tend to rise and produce undesirable optical effects.

On both sides of the equator there are high pressure zones which should be, and indeed have been, found very favourable for astronomical observation. In these zones the incidence of cloud is much lower (Brooks, 1930) and frequent stability or slow settling conditions in the atmosphere favours good seeing.

At the 1948 meeting of the International Astronomical Union it was suggested that an international observatory should be established and located between 10° and 40° south latitude. The requirements for the sites suggested were that it should be noted for its fine seeing, preferably at an altitude of between 6,000 and 10,000 feet, with not less than 225 clear nights per year and no two-month period more than fifty per cent. cloudy. It was admitted that these specifications might be very hard to satisfy, and, although in Australia there would be excellent sites found, the altitude requirement would be a very restricting one. I am inclined to think that the value of an altitude above two to four thousand feet could easily be overrated, provided that tests of seeing and transparency gave satisfactory results. The absorption (photographic, see Buisson *et al.*, 1930) caused by passage horizontally through 3,000 feet of the atmosphere at altitude 1,000 feet would be about 0.04 magnitude and this is a substantial proportion of the absorption at a good astronomical site where the extinction coefficient might be 0.15 mag., and the absorptive capacity of the atmosphere is much greater in its lower layers and varies rapidly with height (Middleton, 1941). It will be seen that only very large increases in altitude of the place will affect the result very materially after, say, 3,000 feet. Australia is very favourably situated in the southern hemisphere, having the largest part of its area in the latitude zone most likely to be favourable, and having large areas with good freedom from cloud. The northern limit for placing the observatory should be more like 25° south latitude, since any further north would place at too great a zenith distance the part of the sky which is most completely inaccessible to northern countries and which it is most essential to observe.

AUSTRALIAN METEOROLOGY FOR ASTRONOMICAL OBSERVATION.

We can now apply the considerations of the previous section to Australia. Figure 1 is a previously unpublished map of "Clear and Cloudy Days", which is included by kind permission of the Director of Meteorological Services (of Australia). I have also to thank Mr. C. J. Wiesener of the Meteorological Bureau at Sydney for assistance with climatological material. It is divided into regions over which the cloud regime remains much the same. By a clear day is meant one which is judged to be equal to or less than two-tenths cloudy, and by a cloudy day one equal to or greater than eight-tenths cloudy. The number of

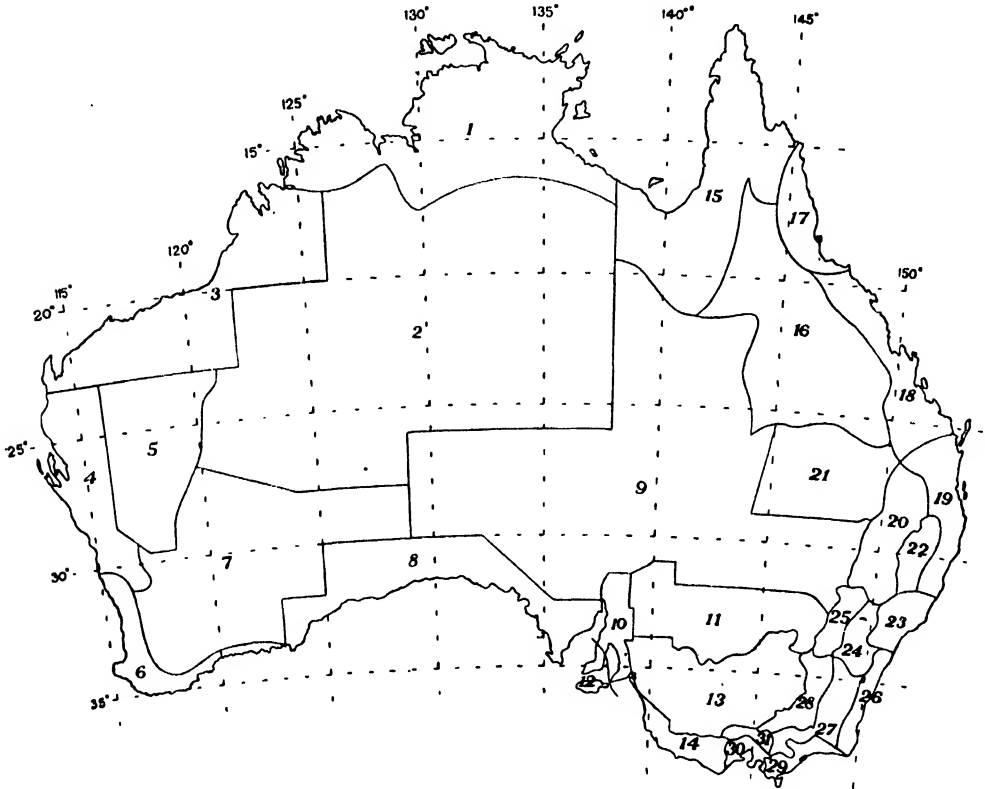


Fig. 1.—Clear and Cloudy Days in Australia.

clear days recorded in each quarter (the first including December, January and February) is given for each region in the first column and the number of cloudy days in the second (bracketed) column.

Another map which is sometimes used to find places which should be free from cloud is one showing the average annual number of days of rain. Such maps are available in a publication by the Meteorological Branch (1945) or by T. G. Taylor (1920). There are large areas in Australia which have less than 30 days of rain in the year but in the areas where living is congenial it might easily be necessary to be satisfied with 60 days. According to the data given by Brooks (1930) a location averaging four-tenths cloudy is a favourable one and, indeed, one as good as this is not likely to be found outside the zones of maximum pressure on either side of the equator. It may be mentioned that when places were being selected for the Harvard stations for observation of meteors it was

| Region. | Quarter | | | Quarter | | | Quarter | | | Quarter | | |
|---------|---------|---------|------|---------|------|------|---------|-------|------|---------|-------|------|
| | Dec. | Jan. | Feb. | Mar. | Apr. | May. | June, | July, | Aug. | Sept., | Oct., | Nov. |
| 1 | | 12 (31) | | 40 (15) | | | 68 (5) | | | 42 (6) | | |
| 2 | | 35 (12) | | 46 (10) | | | 57 (7) | | | 50 (5) | | |
| 3 | | 39 (7) | | 51 (12) | | | 71 (7) | | | 67 (3) | | |
| 4 | | 45 (5) | | 43 (9) | | | 46 (9) | | | 54 (6) | | |
| 5 | | 43 (8) | | 45 (10) | | | 50 (11) | | | 52 (4) | | |
| 6 | | 23 (15) | | 17 (28) | | | 10 (30) | | | 15 (23) | | |
| 7 | | 55 (10) | | 44 (16) | | | 32 (25) | | | 43 (17) | | |
| 8 | | 27 (14) | | 25 (17) | | | 26 (15) | | | 28 (15) | | |
| 9 | | 43 (10) | | 50 (8) | | | 53 (9) | | | 54 (7) | | |
| 10 | | 32 (12) | | 27 (17) | | | 17 (19) | | | 24 (16) | | |
| 11 | | 48 (11) | | 41 (12) | | | 29 (15) | | | 39 (12) | | |
| 12 | | 15 (18) | | 9 (22) | | | 3 (27) | | | 7 (23) | | |
| 13 | | 42 (8) | | 36 (14) | | | 21 (22) | | | 33 (16) | | |
| 14 | | 14 (21) | | 13 (25) | | | 9 (27) | | | 11 (25) | | |
| 15 | | 10 (19) | | 24 (9) | | | 45 (7) | | | 27 (4) | | |
| 16 | | 27 (16) | | 38 (11) | | | 56 (9) | | | 47 (5) | | |
| 17 | | 8 (19) | | 10 (14) | | | 26 (10) | | | 16 (5) | | |
| 18 | | 14 (13) | | 24 (11) | | | 42 (10) | | | 30 (5) | | |
| 19 | | 13 (17) | | 15 (18) | | | 30 (18) | | | 22 (16) | | |
| 20 | | 34 (13) | | 44 (12) | | | 51 (14) | | | 46 (9) | | |
| 21 | | 34 (10) | | 40 (7) | | | 52 (13) | | | 49 (10) | | |
| 22 | | 24 (17) | | 24 (18) | | | 27 (19) | | | 29 (10) | | |
| 23 | | 13 (17) | | 15 (17) | | | 18 (14) | | | 15 (15) | | |
| 24 | | 30 (18) | | 26 (27) | | | 34 (18) | | | 36 (17) | | |
| 25 | | 36 (8) | | 35 (8) | | | 32 (16) | | | 37 (11) | | |
| 26 | | 15 (23) | | 21 (22) | | | 30 (16) | | | 22 (18) | | |
| 27 | | 30 (13) | | 25 (19) | | | 22 (22) | | | 26 (14) | | |
| 28 | | 39 (7) | | 39 (13) | | | 24 (26) | | | 31 (14) | | |
| 29 | | 8 (22) | | 11 (23) | | | 7 (21) | | | 7 (23) | | |
| 30 | | 14 (24) | | 11 (27) | | | 7 (28) | | | 9 (27) | | |
| 31 | | 44 (9) | | 35 (17) | | | 20 (24) | | | 28 (14) | | |

agreed (Whipple, 1949) that an average of about "5.5 hours of clear sky per night is within a few per cent. of maximum clear sky available in North America."

Figure 2 is a map of Australia showing the average daily range of temperature. It should be easy to choose a place in any of the districts otherwise suitable for astronomical work that has a mean daily range of temperature less than 25 degrees, although it must be recognized that the need of a low temperature range is somewhat antagonistic to that of clear skies. However, the requirement of an elevated position does favour a low temperature range.

In regard to wind, little can be said unless specific localities are being examined. In general, the southern part of Australia is subject to westerly winds in the winter time and the northern parts have predominantly south-easterly winds, especially in the autumn and winter. The parts of New South Wales on the western side of the Blue Mountains have a high percentage of calm weather.

The altitude of any district which needs to be considered can, of course, be found approximately from atlases and larger scale maps, which are available from government departments responsible for survey work, and there is no need for the information to be given here.

I believe that the air over Australia is distinguished by high clarity. I have made a few measures of atmospheric extinction during the past year, although not as many as I had hoped, as the period I had set aside for it proved cloudy. A small camera and a guiding telescope were mounted equatorially on a portable stand, the guiding being done by hand without a driving clock. To photograph stars down to the fifth magnitude an exposure of 15 seconds was used. The plate was calibrated by photographing a number of stars near

the zenith with a wide range of magnitude and, when these stars were compared with another group photographed on the same plate at a low altitude, the effect of the atmosphere on the apparent brightness of the lower stars was obtainable. The star images were compared by medium of what has come to be called rather elegantly a "fly spanker".

The results were analysed with the usual formula for atmospheric extinction

$$m_0 = m_1 - k(\sec z - 1)$$

where m_0 is the magnitude at the zenith, m_1 the apparent magnitude, z the zenith distance, and k is the coefficient of extinction determined to give values of m_0 consistent with the tabulated values for the various stars. The list of stars

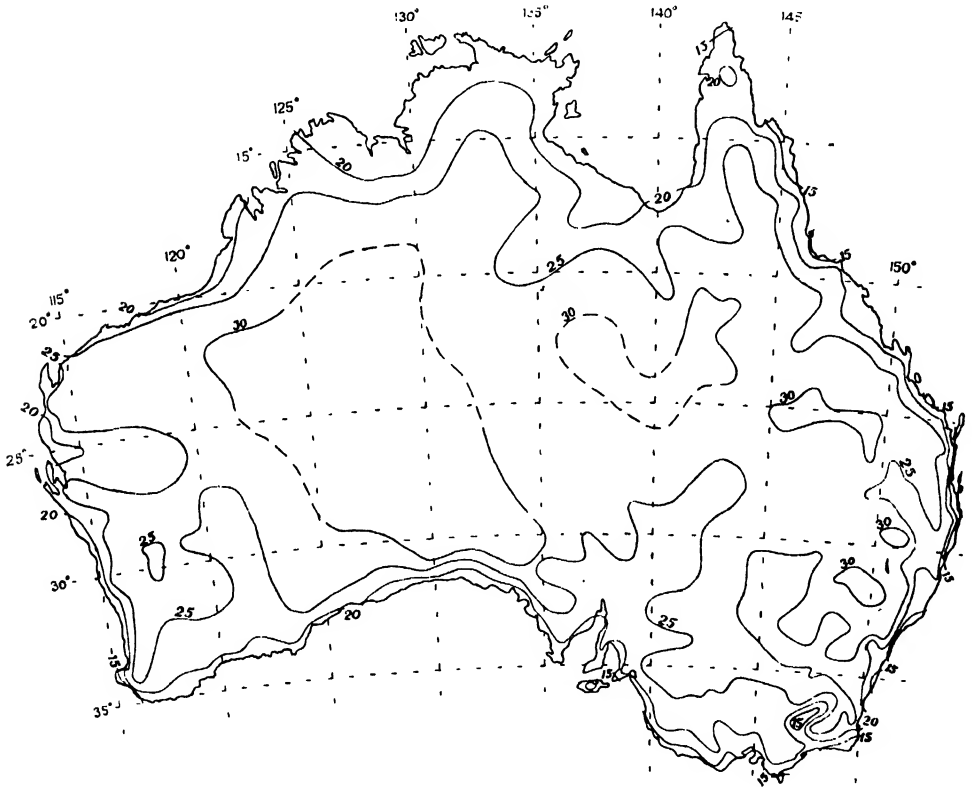


Fig. 2.—Mean diurnal temperature range (average maximum—average minimum) in degrees Fahrenheit. This map and Fig. 1 are published by courtesy of the Director of Meteorological Services.

selected for observation were all in spectral classes B and A, so that it could be hoped that errors in the estimated photographic magnitudes would not affect the result seriously; and this does appear to be the case, especially when the extinction stars are very low and the effects of absorption larger than any error likely to occur. Even if the magnitudes used were not reliable and $\sec z$ not a sufficiently good approximation for the air mass in the formula, a *comparison* between sites would be obtained if the same methods and the same stars were used.

The following table gives the results which were obtained.

| Place. | Long. | Lat. | Height. | Month. | No. of Nights. | k |
|-----------------------------------|--------|--------|---------|------------|----------------|------|
| | ° / | ° / | Ft. | | | |
| Orange | 149 09 | 33 18 | 2,900 | Dec., 1949 | 3 | 0.19 |
| Sydney Obs. .. | 151 12 | —33 52 | 150 | Dec., 1949 | 2 | 0.47 |
| Toronto, N.S.W. . | 151 30 | —33 0 | 50 | Jan., 1950 | 1 | 0.40 |
| Sugar Loaf Trig. Station | 151 30 | —32 54 | 1,300 | Jan., 1950 | 1 | 0.28 |

No comment is necessary on these results except that the values are satisfactorily low, especially as they are in the ordinary photographic wave-lengths. A result similar to the one at Orange was obtained by Woolley and Gascoigne (1948) during their work on the magnitude of the Sun at Mt. Stromlo; this compares favourably with the values at the Lick and Mt. Wilson Observatories (Fath, 1935). The observations at Sydney were made when the sky appeared clear of industrial smoke as well as cloud.

As regards seeing conditions, it must be admitted that our knowledge is not sufficient, but astronomers and surveyors have given good reports of conditions in inland areas. H. C. Russell was enthusiastic about seeing conditions on the mountains west of Sydney, C. J. Merfield commented favourably on conditions at Wee Waa, New South Wales, and W. F. Gale on the seeing conditions at Armidale. Others who have worked in the country, and with whom I have had nights at the telescope in Sydney, have often remarked on the superiority of their atmosphere even on nights regarded as quite satisfactory.

Even such a brief review as this indicates that Australia has localities almost certain to be outstanding as astronomical stations. The districts of Canberra, Armidale, Warwick, Toowoomba and Alice Springs all promise well and if field tests were to be made it would be interesting to compare such an inland town of New South Wales as Dubbo with the others. Observations could also be made, where reasonable transport facilities exist, in regions 4, 5, 7, 9 and 21 of Figure 1: Cue in Western Australia would be one. As far as freedom from cloud is concerned, these areas would be among the best in the world. Canberra has the advantage of having already a flourishing observatory and the Australian National University. These would be of much value to a research institution, as its staff would have the benefit of contact with others working in similar fields and of library facilities beyond those maintained within the institution itself. Of the meteorologically favourable sites, Mt. Stromlo is one of the farthest south, not only in Australia but in the southern hemisphere, with the south celestial pole highest. Armidale is on an extensive plateau with altitudes of more than four thousand feet available close at hand, and is the home of the New England University College. The claim of other places would rest chiefly on their meteorological advantages, or their ability to provide a high frequency of good seeing conditions.

EDUCATION IN ASTRONOMY.

One thing in which astronomy lags in Australia is in education. It is a strange deficiency, for the general public seem very interested and many hundreds visit Sydney Observatory each year. Astronomy is not mentioned in the calendar of several of our universities, and in most, only the astronomy used in connection with surveying is formally taught. At Sydney, it is one of the

choices available to students of mathematics after taking a first degree. Of course, a little astronomy necessarily appears in some other courses, such as physics and geography, and a number of Australian physicists have shown interest in astrophysical applications of their subject. In New South Wales, astronomy has recently been introduced into the secondary schools as a part of a general science course. In many universities in other countries, not only in America, England and Germany, but also in countries which have material resources of the same order as those of Australia, such as Holland or Argentina, astronomy may be taken as a full subject. It has played an exceedingly important part in the history of science, in the growth of scientific method, and in the development of the ideas we have of the universe and the place of world in it; as, for example, by the re-orientation of man's ideas at the time of Copernicus. Once again at the present time I believe a similar re-orientation, possibly attended by less bitterness, is taking place, as astronomy pioneers what may prove to be a knowledge of the structure of the universe as a whole. The discovery of gravity and of the finite velocity of light came from astronomy; and, although the only material which reaches our laboratories from outer space comes in the form of meteorites, one of the elements was first discovered on the Sun by an astronomer. We should not be content while there is no professor or lecturer in astronomy in an Australian university, as for example there is one in meteorology at Melbourne. Apart from the fact that astronomy deserves in its own right a place in tertiary education, some training at that level is necessary in order to equip teachers who will be undertaking teaching at secondary level.

In other countries the association between an observatory and a university has been found stimulating to both institutions, if indeed, an observatory run by a university can be regarded as a separate institution. Many of the observatories of the world are organized in such association, among them being the university observatories of London, Cambridge, Oxford and Glasgow in Great Britain, and nearly all of those of the United States of America. Most of these universities make available courses of study which leave the student with a thorough knowledge of astronomy and, if his inclinations and abilities are so directed, with technical equipment to engage in independent research. The University of Leiden, in Holland, is a famous one of these; and many Dutch astronomers occupy high positions in observatories all over the world. Another university which, to judge by its published plan of studies, gives a very complete and satisfying course in astronomy is the Argentine National University of La Plata, which also has a first rate observatory associated with it. Although I have been speaking of astronomy as a whole, I would like particularly to stress the need for teaching and research in fundamental astronomy, rather than in astrophysics, which appears to be able to look after itself very well. Now if a university department were being established in any subject it would be natural to consider whether its staff, by nature of the organization of the department and of the subject being studied, would have sufficient opportunity to do research work; and since fundamental astronomy has fallen somewhat into the background let me repeat that there are abundant opportunities in this field. Observations of good quality are needed for comparison with the ephemeris positions of various bodies for continual improvement of the astronomical constants; and, on the theoretical side, we must remember that the theories we have are based on observations of the motions of the planets only over a period of a few hundred years and the stability of the Solar System has so far only been studied with simplified assumptions, which may be justifiable in making a first approximation, but not in aiming for a definitive result. The researches of Poincaré form a wealth of material which has never been properly exploited. H. R. Morgan (1946) and G. M. Clemence (1947) in emphasizing

the importance of fundamental astronomy give many examples of recent or much-needed work in this field. Sir Edmund Whittaker (1949) in his article for the celebration of the centenary of the birth of Laplace last year, said :

"It is, in my opinion, to be regretted that at the present time, professional pure mathematicians . . . devote their attention to artificial examples constructed by themselves, instead of trying to solve the vastly more interesting problems of pure mathematics that are presented to us by nature. The remarkable properties of the expansions of Celestial Mechanics have never, so far as I know, been investigated by any of the pure mathematicians who specialize in questions regarding convergence of series."

To illustrate the activity that does exist, we may point to many recent researches in dynamical astronomy, as for example on the two body problem involving subjects such as apsidal motion of binary stars and the distribution of mass within them. Einstein and Infeld have only recently produced the theory of the double stars within the framework of relativity theory and the new knowledge being gained of the atmospheres of close binary stars shows that these give us a problem in dynamics which includes a close examination of the way in which stellar masses might vary and the effect that this would have on the evolution of the binary systems.

I do feel that, although Australia is doing work of which we may be proud, we should look forward to even wider grasping of the opportunities which undoubtedly exist. For this, one of the basic needs is a vital school of astronomy associated, if possible, with an observatory.

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DALTON-GUNNING AREA, N.S.W., EARTH TREMORS OF MARCH, 1949.

By G. F. JOKLIK, B.Sc.

With four text-figures.

Manuscript received, December 15, 1949. Read, April 5, 1950.

I. INTRODUCTION.

On March 11th, 1949, severe earth tremors were felt in the Dalton area, and, less severely, over a considerable portion of New South Wales. These were succeeded in the epicentral area by numerous aftershocks during the following fortnight.

As officers of the Bureau of Mineral Resources, Geology and Geophysics, Canberra, G. M. Burton and the writer were detailed to investigate the tremors, and left Canberra on the first day of their occurrence. The greater part of the week devoted to the investigation was spent in the Dalton area. A reconnaissance embracing an area within a radius of some 40 miles of Dalton was also carried out with a view to determining the regional distribution of intensities, and the Chief Geologist circularized post masters and police officers stationed at fourteen N.S.W. towns from which some information about the tremors was to be expected.

On the party's return G. M. Burton was detailed to another field project and was thus unable to participate in the compilation of this paper.

II. GENERAL DESCRIPTION OF THE EARTH TREMORS.

The first shock, which appears to have been the heaviest in all areas affected, and which caused most of the reported damage, occurred at 8.31 a.m. (*a*), on Friday, 11th March. A strong aftershock was felt at 9.30 a.m. (*b*), and an even more noticeable one shook the epicentral area at 1.33 p.m. (*c*), causing further damage. The last severe aftershock took place at 11.24 p.m. on Wednesday, March 16th (*d*). These four principal shocks were the only ones noted by observers more than seven miles from the epicentral area, and shock (*b*) was felt only in a limited area in a southerly direction from the epicentre.

No preliminary phase preceding the main shock was reported anywhere. Shock (*a*) was very abrupt, and the most reliable estimates of its duration were approximately five seconds. Durations of the same order were assigned to the other principal shocks. The intensity of the main shock in the epicentral area was estimated as VIII on the modified Mercalli scale (see p. 25). The intensity gradient was very steep in all directions away from the epicentre.

The relatively dense population of the epicentral area facilitated the investigation. For almost ten days after the main shock this area was subjected to frequent slight aftershocks, none of them sufficient to cause further damage, although their abruptness caused considerable uneasiness amongst the local inhabitants. During the two or three days succeeding the main shock the aftershocks occurred at roughly half-hourly intervals, and less frequently during the latter part of this period.

III. INSTRUMENTAL DATA.

Riverview Observatory, Riverview, N.S.W., and Brisbane Observatory both recorded the tremors. Unfortunately these are both situated on approximately the same azimuth from the epicentre. For the information given below in Table 1, the writer is indebted to Father D. O'Connell and Mr. P. F. Rheinberger, of the Riverview Observatory.

TABLE 1.
Data from Riverview Observatory.

| Date. | E.S.T. | | | Distance from Riverview. | Azimuth from Riverview. |
|-------------|--------|----|----|--------------------------|-------------------------|
| | h. | m. | s. | Km. | |
| 1949— | | | | | |
| March 11 .. | 8 | 31 | 36 | 190 | 240° |
| | 13 | 33 | 54 | 190 | 240° |
| March 16 .. | 23 | 25 | 24 | 190 | 240° |

The distance and azimuth measurements correspond with an epicentre in the Dalton-Gunning district. The many small aftershocks mentioned in the preceding section were not recorded at Riverview. They appear to have been near-surface phenomena, most of them being accompanied by considerable sound effects.

On the morning of 13th March the party was favourably stationed in a two-story building under a corrugated iron roof at Yass for recording a series of tremors which were felt between 6.15 a.m. and 6.40 a.m. Details of the climax of this set of tremors, which occurred at 6.31 a.m., are recorded in Table 2.

TABLE 2.
Details of Tremors at 6.31 a.m., 13th March, 1949.

| Duration of Tremor (secs.) .. | | | | | | * | | | | | | | |
|-------------------------------|----|----|----|----|----|----|----|----|----|--|--|--|--|
| | 20 | 20 | 40 | 65 | 85 | 60 | 60 | 25 | 20 | | | | |
| Interval (secs.) .. | | 45 | 30 | 25 | 10 | 10 | 15 | 30 | 40 | | | | |

The actual peak is marked with an asterisk, and at that stage a slight bumping of the floor was felt; all the other shocks were gauged by the trembling of the corrugated iron roof. It is seen that, as the climax is approached, the shock period increases. Inversely, the interval between successive shocks decreases. Past the climax, the reverse holds.

IV. EFFECTS OF THE EARTH TREMORS.

(a) *Damage to Property.*

In all, some 150 persons were interviewed, and the properties of most of these were inspected. Press reports drew attention to damage in the township of Dalton itself, but it was found that landholders to the immediate east suffered more heavily.

Damage in the epicentral area included such items as heavily cracked walls, collapse of chimneys, collapse of timber stacks, shifting of heavy machinery,

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collapse of poorly constructed walls, destruction of parapets, bursting of concrete water-tanks, breakage of pictures and property stacked on shelves, etc. The most spectacular damage was of course caused in the most poorly built structures. In the township of Dalton all the more modern buildings with the exception of one concrete edifice escaped serious damage. The Royal Hotel, which had previously been condemned, and the two churches, both very old buildings, received the greater publicity. In these three it was found, upon removal of

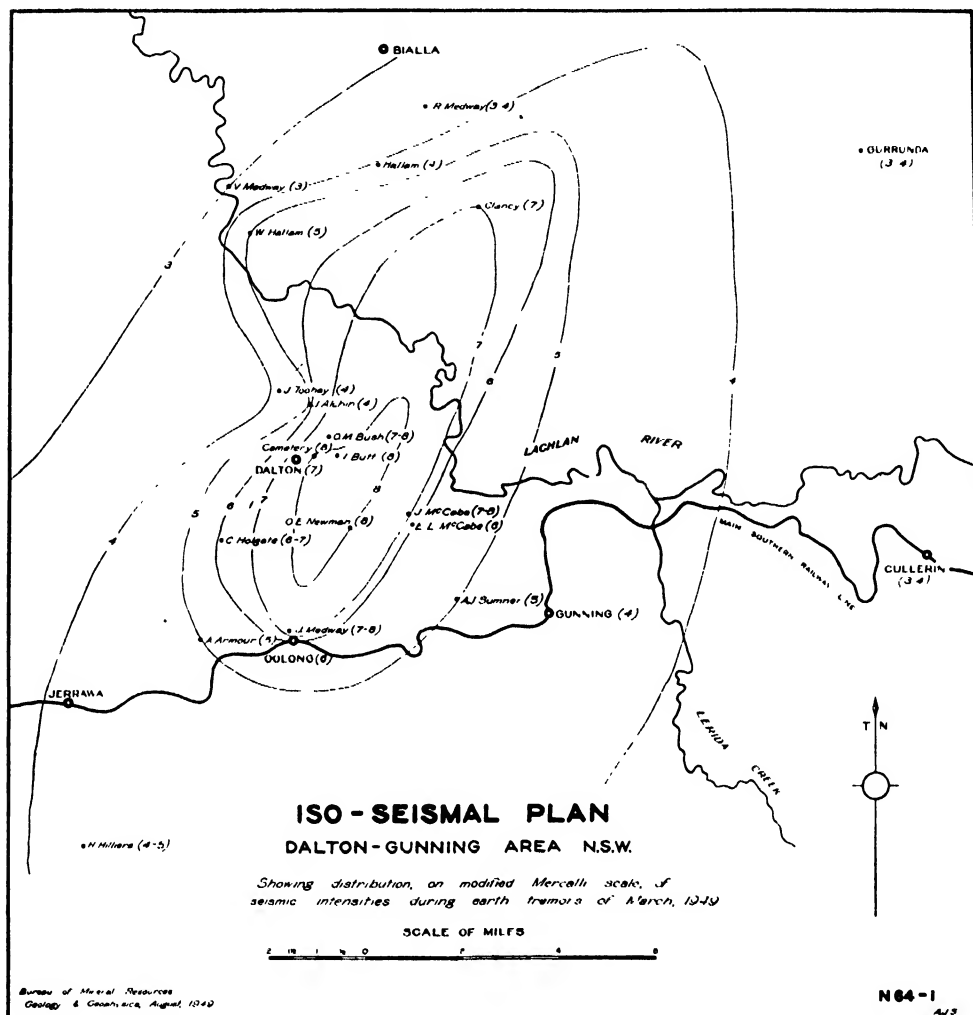


Fig. 1.

the plaster, that the walls were built of irregular granite and sandstone blocks the interstices between which had been filled with mortar, wood, and even paper. Numerous chimneys collapsed in the township, but here again it was found that the cement in most cases had crumbled.

The heaviest, though not the most spectacular, damage was inspected at the properties of O. E. Newman, J. Medway, I. Butt, J. McCabe and at the Dalton Cemetery (see Fig. 1). These define approximately the epicentral area.

At the property of O. E. Newman, sawmiller, the earth tremors produced almost continuous rumblings for several days. A heap of sawdust was overthrown to the east, producing a complex pattern of fractures. Heavy wooden posts supporting the roofs of sheds moved relative to the earth, and the wheels of heavy machinery moved up to six inches in relation to the ground. In an outhouse the basement bricks were shifted by several inches. The brick fireplace was cracked, and all chimneys collapsed.

J. Medway's station homestead is a modern solidly-built brick house on good foundations. Cracks up to one-quarter inch in width, generally at a height of eight to nine feet above the ground, damaged the walls of every room, and large sheets of plaster were removed. Doorways built in a north-south direction were distorted; most objects had indeed been displaced to the north relative to the ground, suggesting that the shocks travelled north to south. Two concrete 2,000 gallon water tanks were fractured at the base, causing one of them to drain completely.

The house of J. McCabe was partly destroyed. It is situated on deeply weathered granite, and is built of loosely-cemented granite blocks. It is suggested that, had the building been of better construction, damage would have been slight.

Undoubtedly the heaviest damage to property was observed at the Dalton Cemetery. Two granite pyramids, four feet high, had been rotated through 20° in a clock-wise direction. Some slabs had been cracked, and in numerous graves the side-stones had moved away from the tombstone by three inches.

Outwards from the epicentral area damage was found to fall off rapidly. Outside a seven-mile radius from Dalton it was confined to an occasional fallen vase or bottle, and inhabitants mostly reported only the rattling of windows and crockery, and swaying of suspended lamps.

The results of the survey of the damage caused by the tremors suggest the following observations with regard to

- (a) the suitability of different building materials in the Dalton area;
- (b) the influence of the geological foundation on damage to buildings.

Faulty or poor construction is naturally associated with the greatest damage—it was this which led to the exaggerated press reports which followed the tremors. Solid and preferably deep foundations were found to be important. In houses of sound construction, the following materials are listed in their order of greatest resistance to shock, according to the present party's field observations:

- (1) Fibro cement,
- (2) Weatherboard,
- (3) Brick,
- (4) Concrete.

In the township of Dalton a concrete cottage which had not even been completed was damaged beyond repair. On the other hand C. Holgate's homestead, although within the epicentral region, showed very little damage; it is built of weatherboard on good foundations. Damage to effects within the house was severe.

The two main rock types in the Dalton area are massive granite and Palaeozoic slate. Generally houses built on granite suffered more than those on slate. For example, the house of J. McCabe, built on granite, was partially destroyed, whereas that of E. L. McCabe, only 600 yards distant, on slate, suffered only slight damage. Two explanations could be given. The first is that the granite, with its deep zone of weathering, provides a less sound foundation than does the compact cleared slate. The second is that the granite, through its rigidity, transmits shock more abruptly than the slate, which, by virtue of its cleavage, is elastic and absorbs some of the shock.

(b) *Surface Effects.*

These included displacement of granite boulders, cracks in the ground, and slippage in alluvial banks.

On a granite hill only a few hundred yards east of O. Newman's house the following phenomena were observed: a granite block measuring $2' \times 3' \times 2'$ was displaced horizontally about three inches. Another block, $2' \times 1\frac{1}{2}' \times 1'$ moved down an inclined plane a distance of six inches. Half a mile south-west of O. Newman's house a block measuring $14' \times 8' \times 10'$ moved along an inclined joint plane, ploughing up the ground and damaging a tree. J. McCabe also reported movement of granite boulders near his house.

Only one crack in the ground was observed, namely on O. E. Newman's property. The trend of the crack was east-west, its length some 18 feet, width one-quarter inch, and the northern side had been displaced to the east a distance of about one-eighth inch. Many inhabitants reported earth cracks which opened during the principal shocks and closed immediately afterwards.

Several slippages of the banks were observed in the creek separating the properties of J. and E. L. McCabe. This dry watercourse is deeply entrenched in thick alluvium and detrital granite. Further minor slippages of this kind were noted in the creeks which spring from the western foot of Bald Hill, two miles east of Dalton.

V. GEOLOGY, PHYSIOGRAPHY AND THEIR RELATION TO THE POSITION OF THE EPI-CENTRAL AREA.

No geological map of the Dalton area was available, and a geological sketch map (Fig. 2) was accordingly compiled from field observations and aerial photographs.

Massive granite, which forms portion of the Gunning batholith, outcrops to the south and west of Dalton. Tertiary basalt flows cap all prominences to the north and west. The country rock is early Palæozoic slate containing beds of shale, sandstone and quartzite. David (1932) assigned an upper Silurian age to these rocks, but the maps published by the N.S.W. Mines Department indicate an Upper Ordovician age. The deposits are of deep-water marine origin and are, apparently, unfossiliferous.

Although the main portion of the granite is massive, definite granitized beds were observed at three localities. The most prominent one follows the chain of hills which trends in a northerly direction through the property of J. McCabe. To the north, roughly a mile to the east of Bald Hill, this granitized bed appears to be faulted out. It is found along the Gunning-Dalton road four miles to the south of Dalton. From the east and west of it, the Palæozoic slate grades into mica schist, strongly banded gneiss, and finally, into a thin band of massive granite.

A similar granitized bed is found along the Gunning-Bialla road, one mile north of the Crookwell turn-off. A remarkable feature of these granitized beds is that the kurrajong tree grows selectively on them. They bear little other vegetation. This peculiarity is apparently related to the original granitized horizons which appear to be offset in places, apparently by faults. This fact has significance in connection with the situation of the epicentral area.

The regional strike of cleavage and bedding is nearly north-south. In detail, variations from this direction are common. The pitch of subsidiary folds is generally to the north.

The western face of Bald Hill is traversed by a strongly mineralized shear-zone, in which the place of the slate is taken by slickenslided phyllite. There is no reason to believe that the shear-zone is connected with any present-day fault-action.

An excellent view is obtained from the summit of Bald Hill. Dalton is situated near the centre of a physiographic basin, some 15 miles in radius. Bald Hill is the highest eminence in a chain of hills which traverses the basin in a north-south direction. The range slopes steeply to the east and west and the faces could actually be termed scarps.

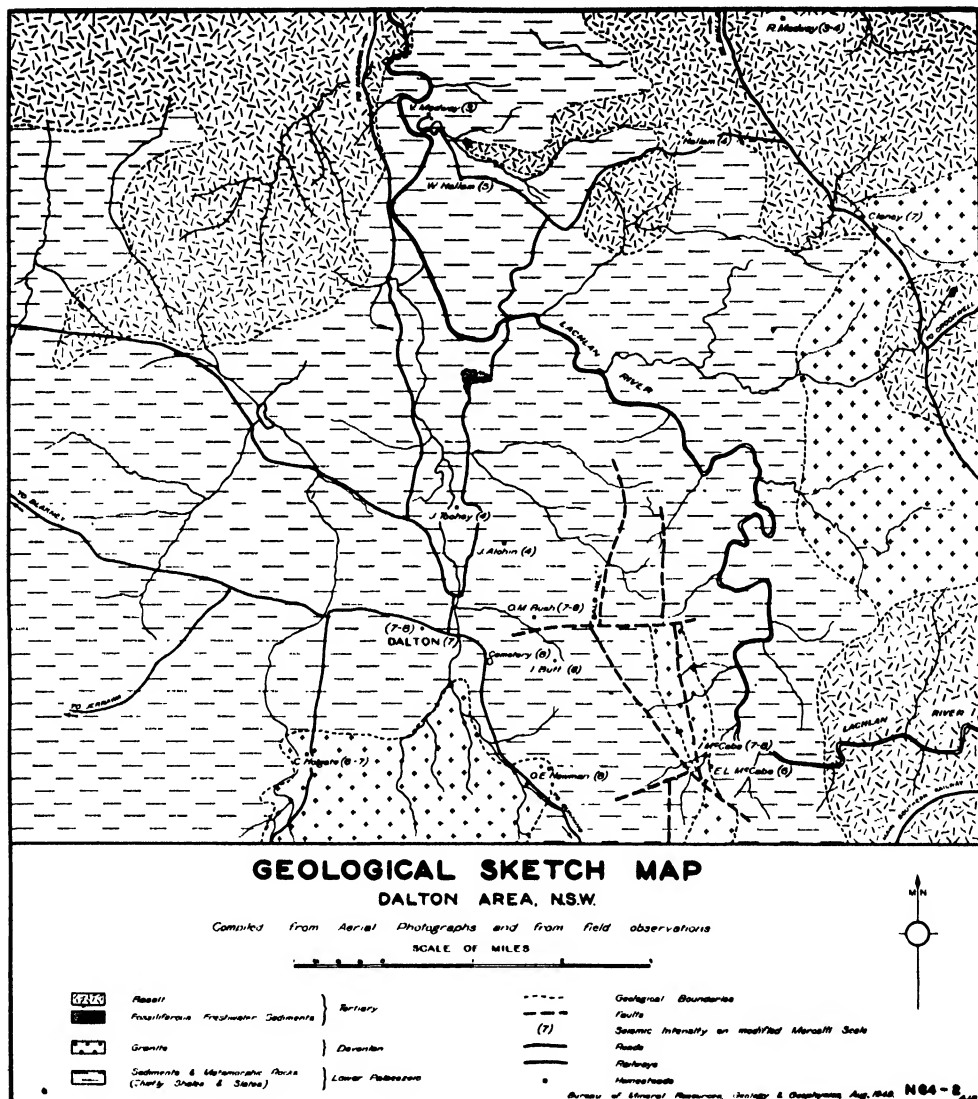


Fig. 2.

The theory is here advanced that the Bald Hill range forms an unstable block which is out of isostatic adjustment with its surroundings, and its efforts to reach isostatic equilibrium are the primary cause of the seismic disturbances in the Gunning-Dalton area.

Except where actual offsetting of the granitized bed was observed, the faults shown on Figure 2 are inserted on physiographic and air photograph

evidence only. Close field examination would be necessary to confirm them. There is little reason to doubt, however, that the "horst" is complexly faulted.

The fact that the chief evidence for some of the faults is physiographic shows that movement must have taken place in recent times. It is suggested

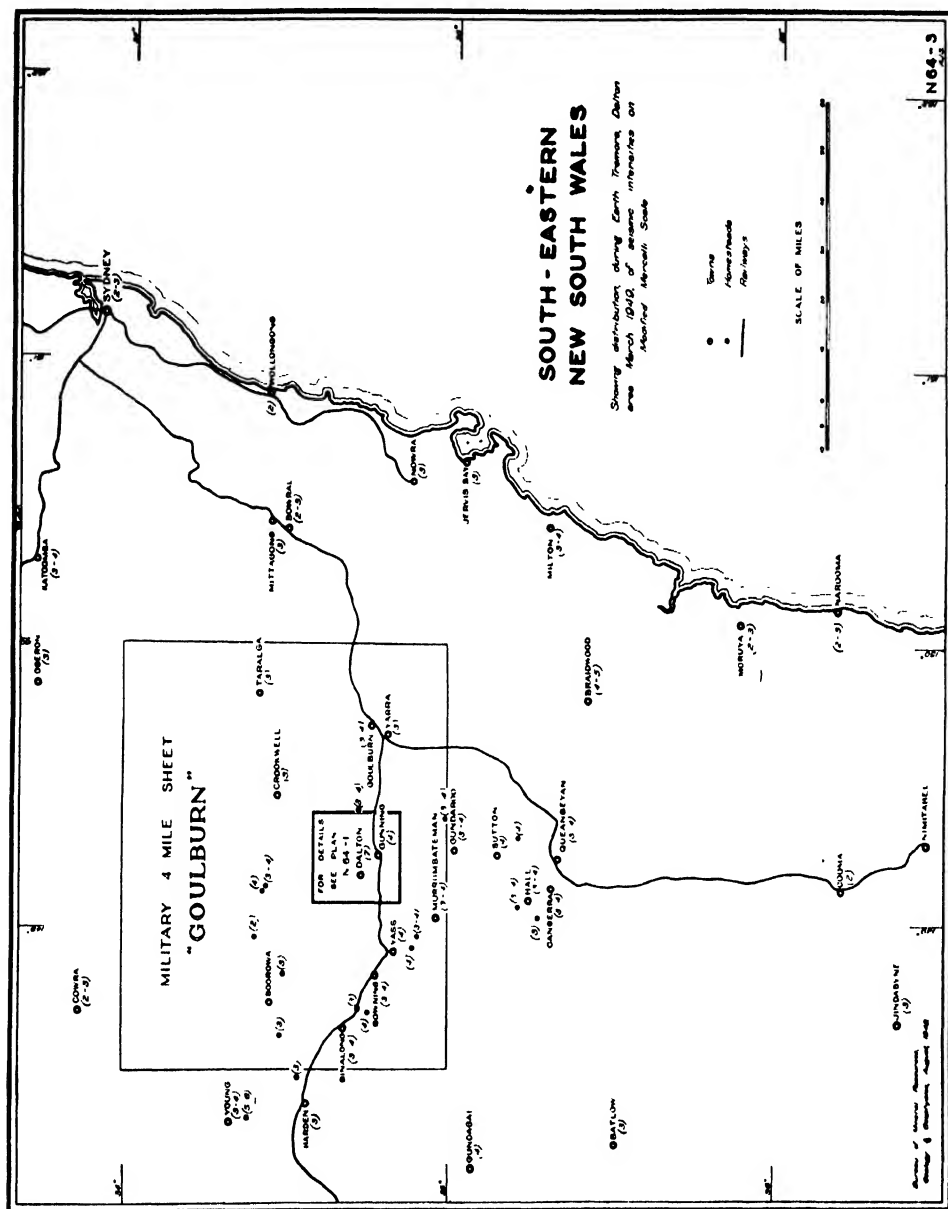


Fig. 6

that such movements are the means by which the "massif" is proceeding towards isostatic equilibrium, and that the cause of the earth tremors is to be found here.

There is one further point of evidence in favour of the theory that the Bald Hill chain is a young upthrust block. It has been stated that this eminence

stands alone in a physiographic basin of considerable radius. To the north and east of Dalton, however, some elevated terrain does exist, and, as is seen from Figure 2, Tertiary basalt forms cappings to it. The base of the basalt is found everywhere at the same altitude, and it seems that the lava was poured out over a peneplain.

Several of the hills in the Bald Hill chain have an altitude considerably in excess of the general basalt level, others are lower, yet nowhere is any sign of basalt found on them. The explanation could be that post-basalt uplift has caused removal by erosion of the lava sheet.

VI. CAUSE OF THE TREMORS AND DEPTH OF FOCUS.

The cause of the tremors experienced in March in the Dalton-Gunning area appears to have been movement along faults in the Bald Hill block. Slight shocks have been felt at roughly six-monthly intervals as far back as the local inhabitants can remember. The process thus seems to be continuous, but at intervals of ten to twenty years relief is given to some residual stresses probably involving movement of greater magnitude.

A shallow focus is indicated by the distribution in time of the tremors and by the rapid falling-off in intensity away from the epicentre (see Figs. 1 and 2). In the case of a deep-seated or even intermediate focus, the Mercalli

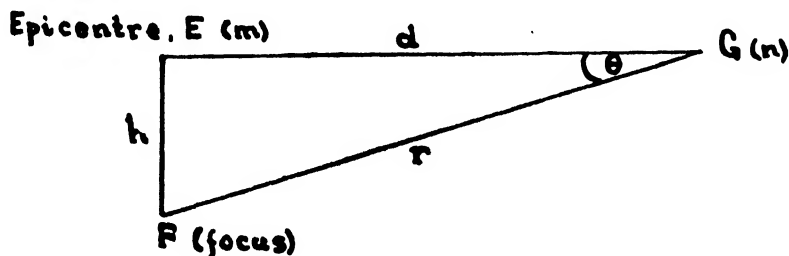


Fig. 4.

values VIII to V (see p. 25) would be expected to cover a far larger area if the seismic disturbance were severe or, if slight, the higher values would be absent and the gradient far less steep. Also the block-faulted Bald Hill chain is not a sufficiently large tectonic unit to have very deep-seated roots.

It has been mentioned that sound effects were prominent throughout the disturbance, which also indicates a near-surface origin for the shocks. Most of the inhabitants, in describing the tremors, spoke of "claps of thunder" and "reports of artillery". The abruptness of the movements supports the same idea. Instead of strong trembling or swaying, the motion took the form of sudden jolts; the former could be expected in a case of deep-focus disturbances, but the latter was the case even in all the innumerable after-shocks.

A rough determination of the focal depth was made by Oldham's method (Holmes, 1946, p. 364). The intensity is expressed in terms of numbers on the modified Mercalli scale (see p. 25). As these are not absolute quantities, an error is introduced.

In Figure 4

- m is the intensity at the epi-centre E ,
- n is the intensity at any other point G ,
- h is the depth of focus.

$$\text{Then } \frac{n}{m} = \frac{h^2}{r^2} = \sin^2 \theta.$$

In the present case, let E be a point midway between O. E. Newman's house and the Dalton cemetery, and let G be at Cullerin (see Fig. 2).

$$\text{Then } \frac{n}{m} = \frac{7}{2 \times 8} = 0.4375 = \sin^2 \theta$$

$$\therefore \theta = 41^\circ 25'.$$

$$\text{Now (Fig. 1) } h = d \tan \theta$$

$$\text{and } d = 19.8 \text{ Km.} = 19.8 \times 0.8821 \\ = 17.5 \text{ Km.}$$

From this the depth of focus would be of the order of fifteen to twenty kilometres, a value which agrees well with the description of the tremors so far given.

VII. THE ISOSEISMAL MAPS.

Throughout this report use is made of the modified Mercalli Scale of Earthquake Intensities. For convenience, a brief summary is included (Holmes, 1946, p. 363).

Intensity.

| | | |
|------|------------|---|
| I | (< 10) | Instrumental, detected only by seismographs. |
| II | (> 10) | Very feeble, noticed only by sensitive persons. |
| III | (> 25) | Slight, felt by people at rest. |
| IV | (> 50) | Moderate, felt by people in motion. |
| V | (> 100) | Rather strong, people are awakened, bells ring. |
| VI | (> 250) | Strong, slight damage. |
| VII | (> 500) | Very strong, cracking of walls, general alarm. |
| VIII | (> 1,000) | Destructive, chimneys fall. |
| IX | (> 2,500) | Ruinous, houses begin to fall. |
| X | (> 5,000) | Disastrous, many buildings destroyed. |
| XI | (> 7,500) | Very disastrous, few structures left standing, ground fissured. |
| XII | (> 9,800) | Catastrophic, total destruction, objects thrown into air, ground badly twisted. |

The numbers in brackets refer to the maximum acceleration of the ground in mm. per sec. per sec.

Figure 1 shows that the isoseismal contours take the form of ellipses where major axes trend in a north-north-westerly direction. They are, in other words, elongated approximately parallel to the Bald Hill chain which appears to be the "seat" of the tremors.

An anomaly is seen to the north-west of the epicentre, in which direction the intensity values fall off abnormally steeply. Figure 2 suggests no geological explanation. Two possible explanations are that:

- (1) a portion of the block-fault system opposite the properties of J. Toohey and J. Alchin did not take part in the recent movements, or
- (2) that the houses of these two landholders were unaffected by the tremors due to some favourable local geological conditions.

The regional map, Fig. 3, showing the distribution of seismic intensities over south-eastern N.S.W., has mainly statistical value. Information was partly obtained by correspondence. Inspection of the map shows that any attempt to contour on this regional scale would have failed, the low Mercalli values are distributed in too irregular a manner, and mostly correspond, in the writer's opinion, to local geological conditions or to different conditions of observation.

VIII. SEISMIC HISTORY.

The first earth tremor recorded from the Dalton-Gunning-Yass area occurred in 1885. Since then Riverview Observatory has recorded many pronounced and slight shocks, and local inhabitants have felt numerous minor tremors which were not strong enough to register at the Riverview.

The last tremors sufficient to cause damage shook the Gunning-Dalton area in 1934. The present party collected information concerning these, and an attempt is made to correlate them with those of March, 1949.

In Table 3 are listed, for comparison, the maximum amplitudes, recorded at Riverview, for the main tremors of 1934 and 1949.

TABLE 3.
Comparison of 1934 and 1949 Earth Tremors.

| Date. | G.M.T. | | | Max. Amplitude (N.-S Movement) (1 μ =0.001 mm.). |
|-------------------|--------|----|----|--|
| | h. | m. | s. | |
| 1934— | | | | |
| November 10 | 23 | 47 | 40 | 40 μ |
| November 18 | 21 | 58 | 42 | 200 μ |
| November 19 | 07 | 10 | 16 | 10 μ |
| November 21 | 06 | 32 | 07 | 80 μ |
| 1949— | | | | |
| March 10 | 22 | 31 | 36 | 170 μ |
| March 11 | 05 | 33 | 54 | 34 μ |
| March 16 | 15 | 25 | 24 | 7 μ |

The figures show that the phase of November, 1934, was more severe and sustained than that of March, 1949. When the local inhabitants were questioned regarding the relative severities, some gave the opinion that the 1934 tremors had greater force, others indicated those of 1949. The 1934 tremors were felt more severely at Gunning, and the Riverview Observatory gives the azimuth of these tremors as 235° and that of the recent ones as 240°, showing that the position of the epicentre for the 1934 tremors was to the south or south-east of that of the 1949 disturbance.

As an example may be quoted the houses of A. J. Sumner, two miles west of Gunning along the Gunning-Dalton road (see Fig. 1). In 1934 the building then in use was so severely damaged that it had to be abandoned. A new house, admittedly of a construction more suited to withstanding shock, was built only two hundred feet from the old one, and during the recent tremors only one chimney was damaged. No additional damage was suffered by the old house.

Enquiries indicated that during the 1934 tremors the zone of greatest damage ran through Sumner's property parallel to the recent epicentral zone.

It is suggested that the cause of both disturbances lay in the Bald Hill fault system. It has been proposed that this system acts in the manner of an active horst, and the theory is now advanced that, whereas in 1949 mainly the western side sought relief, it was the eastern flank which gave way to stress in 1934.

X. CONCLUSIONS AND RECOMMENDATIONS.

The obvious recommendations are that detailed geological mapping be carried out in the area to investigate more closely the possible cause of the

tremors, and that intending builders be made aware of the risk of using unsuitable materials for construction.

Regarding dam construction in the Australian Capital Territory and southern N.S.W., it is not thought that seismic disturbances in the Gunning-Dalton area so far experienced need have any influence on future plannings. The shallow focus and rapid falling-off of intensity indicate that outside a limited radius no damage to such structures is likely.

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PALLADIUM COMPLEXES OF THIOETHERS.

PART I. THE REACTION OF POTASSIUM CHLOROPALLADITE II WITH o-METHYL MERCAPTO BENZOIC ACID.

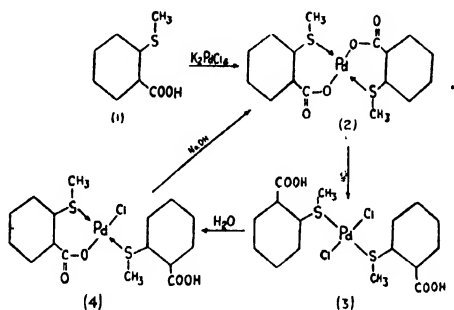
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Manuscript received, March 7, 1950. Read, April 5, 1950.

Amongst the complex compounds formed in the platinum and palladium series those with ammonia and organic sulphides are usually analogous and comparable in properties. Chelating groups such as glycine are well known, and by using this compound *cis* and *trans* forms of diglycine palladium II have been prepared (Wardlaw, Sharratt and Pinkard, 1934).

In the sulphide series, compounds of platinum II with S-ethyl thioglycollic acid ($C_2H_5.S.CH_2.COOH$) have been prepared (Beilstein) but to our knowledge no reaction of this type of chelating molecule with palladium II has been reported.

This investigation deals with the interaction of o-methyl mercapto benzoic acid (1), which functions as a bidentate group, and potassium chloropalladite. Interaction of 2 moles of (1) with 1 mole of K_2PdCl_4 yielded bis (o-methyl mercapto benzoato) palladium II, (2), sparingly soluble in cold water and organic solvents. This compound appeared stable in water and could be recrystallised from boiling water. In the presence of hydrochloric acid, however, the rings were readily opened and the dichloro compound (3), sparingly soluble in water and dilute acid, was formed. Recrystallisation of (3) from boiling water yielded the monochloro compound (4) formed from (3) by the expulsion of 1 mole of hydrochloric acid and the closure of one ring system. With 1 mole of sodium hydroxide in aqueous solution, closure of the second ring occurred, regenerating (2). Tentatively, *trans* structures have been assigned to these compounds.



EXPERIMENTAL.

(1) o-Methyl mercapto benzoic acid.

o-Mercapto benzoic acid, prepared as in Organic Syntheses, was methylated with $(CH_3)_2SO_4$ in alkaline solution. Recrystallised from alcohol-water. M.pt., 168.5–169° C. (Beilstein, 168–169° C.).

Found: S, 18.9%.

Calculated for $C_8H_8O_2S$: S, 19.06%.

(2) *Bis (o-methyl mercapto benzoato) Palladium II.*

K_2PdCl_4 (1.9 g. ≈ 0.006 mole) in 12 mls. of H_2O was added to the cold solution of (1) (1.95 g. ≈ 0.012 mole) in 20 ml. of H_2O and 8 mls. of 2N NaOH. Crude bis (o-methyl mercapto benzoato) palladium II precipitated and became crystalline on standing. Yield, 2.5 g. Recrystallised from boiling H_2O as canary yellow compound consisting of small needle-like crystals, with an acid reaction to litmus paper, and sparingly soluble in cold water and organic solvents. Dried over P_2O_5 ; M.pt. 192–194° C. (decomp.).

Found: Pd, 24.2%; S, 14.4%.

Calculated for $C_{16}H_{14}O_4S_2Pd$: Pd, 24.19%; S, 14.54%.

(3) *Dichloro bis (o-methyl mercapto benzoic acid) Palladium II.*

5.8 g. of (2) were dissolved in the minimum quantity of boiling water (850 ml.) and 50 ml. of conc. HCl added. The yellow solution became dark red and deposited a red-brown crystalline compound. On cooling, a further quantity of (3) crystallised (yield 5.45 g.) in well formed tetragonal prisms, amber in colour and giving an acid reaction on moist litmus paper. The substance decomposed but did not melt at about 240° C.

Found (on separate preparations, dried over P_2O_5): Pd, 20.8%, 20.6%; Cl, 14.0%, 13.7%.

Calculated for $C_{16}H_{14}O_4S_2PdCl_2$: Pd, 20.76%; Cl, 13.80%.

(4) *Monochloro (o-methyl mercapto benzoato) (o-methyl mercapto benzoic acid) Palladium II.*

1.5 g. of (3) were dissolved in boiling H_2O (850 ml.). On cooling crystallisation did not occur and the solution was concentrated at the boiling point to 300 ml. On cooling (4) deposited as fine, bright orange prisms (yield, 1.1 g.), M.pt. 199° C. (decomp.), with an acid reaction on moist litmus paper.

Found: Pd, 22.4%; Cl, 7.1%.

Calculated for $C_{16}H_{14}O_4S_2PdCl$: Pd, 22.34%; Cl, 7.42%.

Regeneration of Bis (o-methyl mercapto benzoato) Palladium II.

0.55 g. of (4) were dissolved in 60–70 ml. boiling H_2O containing 11.5 ml. N/10 NaOH (≈ 1 mole of NaOH to 1 mole of (4)). After concentrating to 40 ml., (2) crystallised on cooling in bunches of thin, yellow needles. Yield, 0.35 g. M.pt., 194°.

Found: Pd, 24.1%.

Calculated for $C_{16}H_{14}O_4S_2Pd$: Pd, 24.19%.

SUMMARY.

The reaction of the sodium salt of o-methyl mercapto benzoic acid ($\equiv SOH$) with K_2PdCl_4 yields the palladium compound $Pd(SO)_2$, yellow crystals. In the presence of dilute HCl the Pd-O links are easily broken, forming the dichloro and monochloro compounds, $(SOH)_2PdCl_2$, amber crystals, and $(SOH)(SO)PdCl$, orange crystals, from which the original compound $Pd(SO)_2$ is regenerated by the action of NaOH.

ACKNOWLEDGEMENT.

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NITROGEN IN OIL SHALE AND SHALE OIL.

XII. THE VOLUMETRIC DETERMINATION OF BASIC NITROGEN IN SHALE OILS.

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INTRODUCTION.

One of the characteristics of shale oils is the presence of basic nitrogen compounds. If these are present in sufficient quantity they may be determined as the decrease in volume of the oil on washing with a dilute mineral acid. However, this method is sensitive to only 0.05–0.1 per cent. of bases by volume (which is the same order as the tar base content of some of the samples), and, moreover, the result is adversely affected by the polymerization of the pyrroles present in the oil (Mapstone, 1948a) and by vapour losses from the volatile samples. In any case the volume of the tar bases is not a direct measure of the basic nitrogen content of the oil as the nitrogen content of the bases decreases with increasing boiling point. A search was therefore made for a more accurate yet simple method.

ACIDOMETRIC METHOD.

Various indicators were examined for their suitability for the acidometric determination of the weakly basic tar bases in aqueous solution. Purified samples of tar bases were analysed for total nitrogen by the modified Kjeldahl method (Mapstone, 1948b), and for basic nitrogen by dissolving various amounts in standard sulphuric acid and back titrating with standard sodium hydroxide solution using the different indicators. Screened methyl orange was thus shown to be the most suitable (Table 1), xylene cyanol FF as the screening agent giving sharper endpoints than methylene blue.

TABLE 1.

Comparison of Indicators for Acidometric Determination of Nitrogen Content of Tar Bases.

(Results as Percentage Nitrogen by Weight.)

| Method. | Sample A. | Sample B. | Sample C. |
|--|-----------|-----------|-----------|
| Kjeldahl | 8.20 | 8.69 | 10.62 |
| Back titration of acid solution using— | | | |
| Screened methyl orange .. | 8.19 | 8.74 | — |
| Bromthymol blue | 8.11 | 8.46 | — |
| Methyl orange | 7.60 | 7.88 | — |
| Screened methyl red | 6.62 | 8.36 | — |
| Methyl red | 6.46 | 7.80 | — |
| Phenolphthalein | — | — | 1.09 |

Several hydrocarbon samples were extracted several times with standard acid and then water washed, the extracts and washings being bulked and aliquots titrated. The results thus obtained were satisfactory but sometimes the extraction was incomplete or sharp separation of the oil and acid was difficult so further work was carried out to overcome these difficulties.

TWO INDICATOR TITRATION.

A technique was sought to determine the weakly basic tar bases by the use of a two indicator titration analogous to that frequently employed for the determination of weak acid such as phosphoric and carbonic acids.

Preliminary experiments showed that screened methyl orange could be used as one indicator. Since the bases were slightly alkaline to phenolphthalein (Sample C, Table 1), and the orange colour of the acid extracts of all but the least discoloured samples interfered with the observation of that endpoint, the requirements of the second indicator were that its colour change be from colourless or yellow in acid solution to blue or green in alkali, and that its pH range be somewhat higher than that of phenolphthalein. Of those indicators which came close to these requirements thymolphthalein was found to be the most suitable.

Aliquots of a solution of a known weight of redistilled tar bases (from the gasoline) in dilute hydrochloric acid were rendered alkaline to thymolphthalein by the addition of an excess of barium hydroxide solution, followed by titration with standard hydrochloric acid, first to the thymolphthalein endpoint, and then to the screened methyl orange endpoint. (This procedure was adopted to prevent the colour of the screened methyl orange from interfering with the other indicator.)

The results, when expressed as the basic nitrogen content of the bases, were high but reproducible. This was found to be due to the need of a blank titration to allow for the wide pH range between the two endpoints (3.7–9.5). This blank ranged from 0.2 to 0.4 ml. of 0.1N acid depending on the volume of the solution being titrated. When this allowance was made the basic nitrogen content (10.82%) was in close agreement with the total nitrogen content (10.62%) as determined by the modified Kjeldahl method.

The method worked satisfactorily for the determination of the bases from the gasoline but was not suitable for the higher molecular weight bases from the light recycle oil from the cracking plant, as the precipitation of the bases interfered with the observation of the endpoint. This interference, some features of which suggested that the precipitated bases may have extracted the indicator from the solution, was overcome by the addition of sufficient methyl or ethyl alcohol (generally about half the volume of the solution) to prevent the precipitation. This was further assisted by keeping to a minimum the total volume of the solution being titrated.

EXTRACTION OF BASES FROM OIL SAMPLES.

In general it was found that two washes with hydrochloric acid were sufficient to extract all the bases from an oil sample provided that an excess of acid was present in each extract. With sulphuric acid it was necessary to have at least a 50 per cent. excess presumably because of the relatively weak second dissociation constant. The concentration of acid employed was relatively unimportant as long as there was an excess present at the last two, or preferably three washes. For samples containing less than 0.1 per cent. of basic nitrogen by weight 100–250 ml. samples could be conveniently extracted with 0.1N acid, but higher tar base concentrations were more conveniently extracted with approximately normal acid.

The technique found most suitable for an unknown sample was to extract a measured volume of the sample (100–250 ml.) with successive portions of 40, 20, 20, and 10 ml. of approximately 1N hydrochloric acid. (If the sample were known to have a low tar base content 0.1N acid could be used.) The extracts were bulked and made up to 100 ml. with distilled water; 10 ml. aliquots were rendered alkaline to thymolphthalein by the addition of a slight excess of barium hydroxide solution after the addition of 20–25 ml. of methyl or ethyl alcohol (necessary only with samples heavier than gasoline or with a very high tar base content). The solution was then titrated with 0.1N hydrochloric acid till the colour of the thymolphthalein was just discharged; four drops of the screened methyl orange were added and the titration continued to the second endpoint. If the second part of the titration required less than 5 ml. of acid it was repeated with a larger aliquot. A blank titration was then carried out using an equal volume of distilled water in place of the acid extract. The basic nitrogen content of the oil sample was then calculated as:

$$\frac{1.4N (T-B)A}{V.D.E.} = \text{per cent. by weight of basic nitrogen in sample}$$

where T=ml. acid required between indicators for aliquot,

B=ml. acid required between indicators for blank,

N=normality of acid,

A=ml. of aliquot titrated,

E=final volume of acid extract (normally 100 ml.),

V=ml. of oil sample taken,

D=density of oil sample.

TABLE 2.

Basic Nitrogen Content of Some Shale Oil Fractions.
(Results of Duplicate Analyses.)

| Sample. | Basic Nitrogen. (Percentage by Weight.) |
|---------------------------|--|
| Crude shale naphtha | 0.016, 0.017 |
| Cracked shale gasoline— | |
| I | 0.0399, 0.0401 |
| II | 0.0266, 0.0270 |
| Topped gasoline— | |
| I | 0.0633, 0.0637 |
| II | 0.0760, 0.0769 |
| Recycle light oil— | |
| I | 0.439, 0.431 |
| II | 0.655, 0.655 |
| III | 0.448, 0.451 |
| Crude shale oil | 0.146, 0.146 |

OXIDIZED OIL SAMPLES.

On standing oil samples tend to oxidize and discolour. Part of this colour was extracted by the acid and interfered with the observation of the thymolphthalein endpoint. Distillation of the oil samples before extraction was found to overcome this difficulty, the colouring materials being left in the distillation residue (0.5–1.0 ml.) which was shown to contain a negligible amount of bases. Discoloured samples were therefore redistilled before analysis.

CRUDE OIL SAMPLES.

Because of its wide boiling range crude shale oil could not be redistilled before analysis and the colour of the acid extract seriously interfered with observation of the thymolphthalein endpoint even when sufficient alcohol had been added to prevent precipitation of the bases, though it did not interfere significantly with the phenolphthalein endpoint. Further work showed that, with the crude oil bases, both these indicators gave the same endpoint, and that direct titration of the acid solution gave more consistent results. The crude shale oil tar bases were therefore determined in the acid extract by titrating alternate aliquots with standard carbonate-free alkali (e.g. barium hydroxide) to phenolphthalein and screened methyl orange endpoints, the tar bases being equivalent to the difference between the two sets of titrations.

Titration of the acid extract to the first permanent precipitate of tar bases required from 0.1 to 0.4 ml. more alkali than titration to the screened methyl orange endpoint and, by not diluting the acid extract before titrating the difference between the two methods of determining the excess acid could be taken as 0.2 ml. of 0.1N alkali when titrating 5-10 ml. aliquots. In this manner it is possible, if necessary, to make both the necessary titrations on the same aliquot.

SUMMARY.

A simple volumetric method has been derived for the determination of the basic nitrogen content of shale oil samples, based on a two-indicator titration of an acid extract.

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NITROGEN IN OIL SHALE AND SHALE OIL.

XIII. AN APPROXIMATE METHOD FOR DETERMINING PYRIDINE NITROGEN IN OIL SHALE AND SIMILAR MATERIALS.

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INTRODUCTION.

Various workers have observed that, for the determination of the nitrogen in pyridine type compounds by the Kjeldahl method, additional digestion time was required after the mixture cleared (e.g. Shirley and Becker, 1945; Cole and Parks, 1946). It was previously suggested by the author that this time factor might be able to be used as the basis of an approximately quantitative method for the determination of pyridine rings in an unknown material (Mapstone, 1948a). This paper presents the results of work carried out to test this hypothesis. Although they do not bear out their initial promise of an accurate quantitative method, it is felt that, as a qualitative and approximately quantitative method, they may be of interest.

WORK DONE.

The apparent nitrogen content of a number of nitrogen compounds of known structure was determined by the modified Kjeldahl method (Mapstone, 1948) for various times of after-boil (i.e. digestion beyond that required for the digestion mixture to clear). The results obtained (Table I) indicate that, in most cases, the oxidation was nearly complete after an after-boil of half an hour. At the end of one hour only those containing a pyridine nucleus or a reduced pyridine nucleus were incompletely oxidized. Of these, only pyridine itself was incompletely oxidized after two hours after-boil.

The proportion of the pyridine nitrogen evolved as ammonia after one hour's after-boil ranged from 60 per cent. for pyridine to 91 per cent. for acridine and isoquinoline. As a first approximation the proportion of the nitrogen evolved appeared to be a function of the amount of substitution in the molecule, but it was not possible to derive any quantitative relationships.

Somewhat similar results were obtained with the much milder digestion conditions obtained by not adding sodium sulphate to the sulphuric acid (Table I), to increase the temperature of the digestion, the pyridine ring compounds yielding from four to 42 per cent. of their nitrogen as ammonia with two hours' after-boil. Quinine (which contains both a pyridine and a quinuclidine nucleus) yielded 64 per cent. and piperidine gave 54 per cent. of its nitrogen in the same time. The other compounds examined which were not completely oxidized under these conditions were indole and its derivatives (80-92 per cent.) and some of the tertiary amines (69-100 per cent.).

APPLICATION OF RESULTS.

Since only pyridine type compounds were not completely oxidized with an after-boil of one hour in the presence of sodium sulphate, this method can be used for indicating the presence of pyridine rings in an unknown material.

TABLE I.
EFFECT OF AFTER-BOIL ON NITROGEN LIBERATED.
(Results quoted as Percentage of Total Nitrogen.)

| | With 30 gm. Sodium Sulphate. | | | | | | | No Sodium Sulphate Added. | | | | | | | Error in Calculated Pyridine Nitrogen, Per Cent. Na ₂ SO ₄ . | | Remarks on Digestion. |
|--|------------------------------|----------|-------|----------|-------|----------|-------|---------------------------|-------|----------|-------|----------|-------|----------|--|------|--|
| | With 30 gm. Sodium Sulphate. | | | | | | | No Sodium Sulphate Added. | | | | | | | Error in Calculated Pyridine Nitrogen, Per Cent. Na ₂ SO ₄ . | | |
| | With. | Without. | With. | Without. | With. | Without. | With. | Without. | With. | Without. | With. | Without. | With. | Without. | | | |
| Digestion time after clearing—hours .. | | | | | | | | | | | | | | | | | |
| COMPOUNDS. | | | | | | | | | | | | | | | | | |
| PYRIDINES— | | | | | | | | | | | | | | | | | |
| Pyridine .. | 48 | 3 | 60 | 86 | 96 | 100 | 45 | 32 | 34 | 29 | 32 | — | — | — | —140 | —9 | No colour change after boil from cessation of frothing. |
| Shale Tar Bases .. | 34 | — | 79 | 99 | 100 | 100 | 13 | — | 17 | — | 26 | — | — | — | +21 | —1 | Normal. |
| Quinoline .. | 13 | 24 | 75 | 100 | 100 | 100 | 1 | — | 4 | — | 18 | 24 | — | — | —11 | +9 | Normal. |
| Isoquinoline .. | 15 | 65 | 91 | 99 | 100 | 100 | 1 | 26 | 27 | 31 | 42 | — | — | — | —52 | —23 | Normal. |
| Quinaldine .. | 23 | — | 72 | 87 | 100 | — | 1 | — | 2 | — | 4 | — | — | — | —59 | +29 | Normal. |
| Acridine .. | 23 | 45 | 91 | 100 | — | — | 4 | — | 16 | 23 | 27 | — | — | — | —55 | n.d. | Normal. |
| 8-Hydroxy Quinoline .. | 55 | 45 | 83 | 100 | 100 | — | 49 | 55 | 57 | 64 | 64 | — | — | — | +12 | —52 | Normal. |
| Quinine .. | 55 | 45 | 83 | 100 | 100 | — | 100 | 60 | 48 | 52 | 54 | — | — | — | —8 | —23 | No discoloration after boil from cessation of effervescence. |
| Piperidine .. | 86 | 43 | 85 | 98 | 100 | — | — | — | — | — | — | — | — | — | — | — | Normal. |
| PYRROLES— | | | | | | | | | | | | | | | | | |
| Indole .. | 94 | 98 | 100 | — | 100 | — | 71 | 85 | 87 | — | 92 | — | — | — | NII | +12 | Normal. |
| 2-Methyl Indole .. | 92 | 97 | 100 | 100 | — | — | 65 | 65 | 71 | 82 | 80 | — | — | — | NII | +27 | Normal. |
| Carbazole .. | 90 | 100 | 100 | — | — | — | 68 | 100 | 100 | 100 | 88 | — | — | — | NII | +16 | Normal. |
| Indigo Carmine .. | 76 | 100 | 100 | — | — | — | 100 | 100 | 100 | 100 | 100 | — | — | — | NII | NII | Normal. |
| Chlorophyll .. | 99 | 100 | — | 100 | — | — | n.d. | n.d. | n.d. | n.d. | n.d. | — | — | — | NII | n.d. | Normal. |
| SECONDARY AMINES— | | | | | | | | | | | | | | | | | |
| Di n-butylamine .. | 87 | 97 | 100 | — | 100 | — | 87 | 88 | 85 | 92 | 97 | 100 | — | — | NII | +4 | Normal. |
| Di n-octylamine .. | 91 | 96 | 100 | 100 | — | — | 86 | 80 | 84 | 93 | — | — | — | — | NII | NII | Normal. |
| Thioethylaniline .. | 79 | 97 | 100 | 100 | — | — | 79 | 93 | 96 | 100 | 100 | — | — | — | NII | — | Normal. |
| Indanthrene Blue .. | 79 | 100 | 100 | — | — | — | 89 | 95 | 100 | 100 | 100 | — | — | — | NII | — | Normal. |
| TERTIARY AMINES— | | | | | | | | | | | | | | | | | |
| Triphenylamine .. | 57 | 78 | 100 | 100 | 100 | — | 44 | 50 | 57 | 64 | 73 | — | — | — | NII | +86 | Normal. |
| Dimethyl Aniline .. | 84 | 100 | 100 | 100 | — | — | 83 | 85 | 96 | 100 | 93 | — | — | — | NII | +9 | Normal. |
| Tri n-Butylamine .. | 82 | 95 | 100 | 100 | 100 | — | 80 | 88 | 90 | 92 | 93 | — | — | — | NII | — | Normal. |
| N N' Diphenyl-piperazine .. | 93 | 100 | 100 | 100 | 100 | — | 60 | 61 | 65 | 67 | 69 | — | — | — | NII | +40 | Normal. |
| MISCELLANEOUS— | | | | | | | | | | | | | | | | | |
| Antipyrine .. | 71 | 74 | 78 | 73 | 72 | — | 82 | 91 | 88 | 87 | 80 | — | — | — | — | — | Gaseous nitrogen evolved during digestion. |
| Cyanuric Acid .. | 100 | 100 | 100 | — | — | — | 91 | 89 | 100 | — | 100 | — | — | — | NII | NII | Remarks as piperidine. |
| Melamine Formaldehyde Resin .. | 79 | 100 | 100 | — | — | — | 58 | 80 | 90 | 100 | 100 | — | — | — | NII | NII | Remarks as piperidine. |
| Uric Acid .. | 80 | 95 | 100 | — | — | — | 64 | 80 | 96 | — | 100 | — | — | — | NII | NII | Digestion time × 3. |
| Gelatine .. | 99 | 100 | 100 | 100 | — | — | 89 | 95 | 98 | 100 | — | — | — | — | NII | NII | Normal. Digestion time × 3. |
| SHALES AND PRODUCTS | | | | | | | | | | | | | | | | | |
| Shale .. | 87 | 94 | 98 | 99 | 100 | 100 | 70 | — | 76 | 85 | 91 | — | — | — | 12 | 12 | Normal. |
| Crude Shale Oil .. | 76 | 87 | 94 | 100 | 100 | 100 | 71 | — | — | 75 | 67 | — | — | — | 36 | 44 | Normal. |
| Petroleum Coke .. | 89 | 98 | 99 | 100 | 100 | 100 | — | — | — | — | 77 | — | — | — | 6 | 31 | Normal. |

The three-fold range from nine to 28 per cent. of pyridine nitrogen not evolved from the samples (other than pyridine itself) means that it cannot be used for accurate quantitative work though roughly quantitative results could be obtained by assuming that one-sixth (16.66 per cent.) of the pyridine nitrogen remained undigested under these conditions. The error in determining in this manner the pyridine nitrogen content of the samples tested is also listed in Table I. This method (Method A) gave errors ranging from -52 to +21 per cent. with the exception of the case of pyridine itself.

In the absence of added sodium sulphate, some materials other than pyridine compounds were incompletely oxidized by an after-boil of two hours. The error obtained by assuming that only one-quarter of the pyridine nitrogen was evolved under these conditions and neglecting other types of compound is also listed in Table I. This method (Method B) gave errors ranging from -52 to +40 per cent.

When applied to complex unknown samples, these approximate methods must be used with caution. The pyridine nitrogen content of crude shale oil, oil shale and petroleum coke, as determined by these two approximate methods, is given in Table II.

TABLE II.
Calculated Proportion of Pyridine Nitrogen in Various Samples.
(Results presented as percentage of total nitrogen content.)

| Sample. | Total Nitrogen. | Proportion of Pyridine Nitrogen. | | |
|-----------------------|-----------------|----------------------------------|-----------|--------------|
| | | Method A. | Method B. | Known. |
| Oil shale | 0.893% | 12% | 12% | Unknown. |
| Petroleum coke | 1.630% | 6% | 31% | Unknown. |
| Crude shale oil | 0.520% | 36% | 44% | Approx. 30%. |

By both methods of calculation, the pyridine nitrogen content of the crude shale oil is slightly greater than the known basic nitrogen content of the oil (Mapstone, 1948b), but the small difference is well within the range of error observed with the pure pyridine compounds.

With the crude oil, and more particularly with the petroleum coke, Method B gave higher results than Method A. This may possibly indicate the presence of indole or stable tertiary amine structures in addition to the pyridine rings in these materials. The pyridine nitrogen content of the oil shale by either method was calculated to be 12 per cent. of the total nitrogen content. Since both methods give the same result the figure can be taken as of the correct order with a reasonable degree of confidence.

DISCUSSION.

This work confirms the relatively slow oxidation of the pyridine nucleus under the conditions of the analysis, as previously shown by the isolation of pyridine carboxylic acids from the Kjeldahl digestion products of coal (Beet and Belcher, 1938). The very slow attack of sulphuric acid on pyridine was shown by the fact that, even after two hours' after-boil in sulphuric acid without added sodium sulphate or one and a half hours in its presence, some pyridine was still distilled with the ammonia on rendering the mixture alkaline. This factor similarly affected the results with piperidine, most of which appeared to be initially oxidized to pyridine, and explains the relatively high results obtained

with both these materials after short digestion periods. Since the pyridine was first converted to a non-volatile and slowly oxidized compound, it is likely that the slowness of the oxidation is due to the difficulty of the further oxidation or sulphonation of pyridine sulphonic acid. The substitution of the pyridine nucleus as in its homologues and benz-derivatives appeared to facilitate the oxidation process as shown by the fourfold range of unoxidized material remaining after an hour's after-boil in the presence of sodium sulphate.

The reasons for the variations observed in the results appear to be mainly due to the effect of the molecular structure but it is probable that other factors, such as the rate of heating etc., are involved. For example, Crossley (1935) found that maximum nitrogen figures were obtained with the minimum heating rate to give the minimum "clearing" time, though no such relationship was observed in the author's previous work on the determination of the nitrogen content of oil shale and shale oil (Mapstone, 1948a). In the work reported in this paper, the heat input to the digestion was controlled to cause the sulphuric acid vapours to reflux in the bottom of the neck of the digestion flask, and was therefore approximately constant. It was noticed, however, that several-fold variations of the clearing time were sometimes obtained though the heating rate appeared to be constant.

Another factor in the application of the results is the absolute accuracy of the analytical method upon which the approximate methods of calculation are based. Duplicate analyses normally checked within one per cent. of the total nitrogen content for the complete digestion, but the accuracy was somewhat poorer when the digestion was incomplete. Assuming that the average accuracy of the analyses was two per cent. of the total, the possible error of the estimate of the pyridine nitrogen content of an unknown sample is twelve per cent. of the total nitrogen content. This possible source of error is somewhat reduced if the duplicate analyses check well with one another, a feature of the analysis of some materials but not of others.

SUMMARY.

Approximately five-sixths of the pyridine ring nitrogen in a sample are oxidized after an after-boil of one hour under standard conditions of the Kjeldahl method, the complete digestion requiring between one and a half and two hours. No other type of nitrogen compound examined interfered, so, in addition to being a qualitative method for detecting pyridine rings in an unknown substance, it can be used as the basis for a very approximate quantitative method. Similar results can be obtained by eliminating the sodium sulphate from the digestion mixture, but some other compounds interfere.

ACKNOWLEDGEMENTS.

The author wishes to acknowledge with thanks the assistance of Mr. R. M. Gascoigne in providing specimens of some of the chemicals analysed, the technical assistance of Mr. R. J. Dibley in carrying out this work, and the permission granted by the Management of National Oil Proprietary Ltd. for the publication of this paper.

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STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

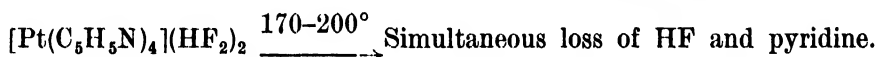
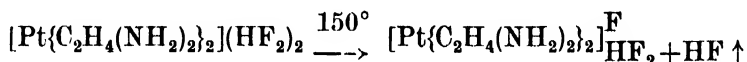
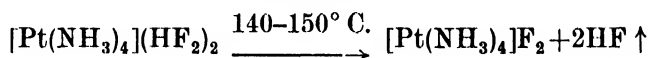
PART II. SOME PROPERTIES OF TETRAMMINE PLATINUM II FLUORIDES.

By R. A. PLOWMAN, B.Sc., A.S.T.C. (Chem.).

Manuscript received, March 7, 1950. Read, April 5, 1950.

In the previous communication (Plowman, 1949) the preparation of the fluorides and hydrogen fluorides of the tetrammine platinum II type was described. This communication reports the decomposition of these compounds on heating.

The results indicate that each tetrammine decomposes in a characteristic manner, which is related to the nature of the coordinating molecule attached to the platinum atom. The results can be represented thus :

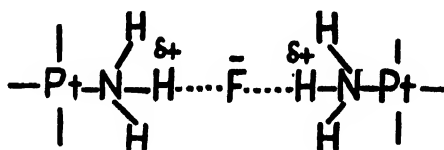


In the ethylenediamine compound the remaining mole of hydrofluoric acid is held strongly, and on heating to higher temperatures no further evolution could be detected. The stability of this compound compares with the compound

$[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\overset{\text{F.H}_2\text{O}}{\text{HF}_2}$ obtained by crystallisation from aqueous hydrofluoric acid and acetone (Plowman, *loc. cit.*).

The hydrated and anhydrous tetrammine platinum II fluorides decomposed completely at temperatures above 200° C. However, if the heating was conducted cautiously, the evolution of some ammonia could be detected at temperatures of $180-200^\circ \text{ C.}$ Tetrapyridine platinum II fluoride 3-hydrate commenced to lose pyridine above 100° C. and at 140° C. the loss corresponded closely with that of 2 moles of pyridine.

The above results are in reasonable accord with the known order of stability of the platinum-nitrogen bonds and with the structures which could reasonably be assigned to these compounds. Thus it is reasonable to expect hydrogen bonding to occur in $[\text{Pt}(\text{NH}_3)_4]\text{F}_2$ analogous to the type occurring in ammonium fluoride which crystallizes with the Wurtzite structure (Wells, 1945). In metal amines the difference in the electro-negativities between the nitrogen and hydrogen atoms permits of a considerable portion of the positive charge on the ion to be drained off to the hydrogen atoms (Pauling, 1948). Such a charge distribution would favour hydrogen bonding and contributions from structures such as



would be expected in $[\text{Pt}(\text{NH}_3)_4]\text{F}_2$. With the replacement of one hydrogen atom by an ethylene group such a symmetrical distribution would not be expected, leading to greater stability of hydrogen fluoride groups in the structure.

The decomposition of the fluoride and hydrogen fluoride of $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]^{++}$ indicate that stable compounds of the dipyridine series are formed. These are being investigated further and will be reported in a communication on the reaction of *cis* and *trans* $[(\text{C}_5\text{H}_5\text{N})_2\text{Pt}(\text{OH})_2]$ with hydrofluoric acid.

EXPERIMENTAL.

All reactions involving fluorides were carried out in platinum vessels.

The Action of Heat on $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2]_2(\text{HF})_2$.

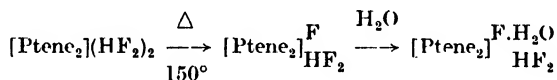
At 103° C. evolution of hydrofluoric acid perceptible and at 150° C. hydrofluoric acid was issuing freely. A temperature of 165° was reached and the issue of hydrofluoric acid ceased after a few minutes. The crystals had lost their clear appearance and were white and powdery.

Found : Loss in weight, 4.2%.

Loss of 1 mole of hydrofluoric acid requires 5.1% ; 2 moles, 10.2%. In another experiment the compound was held at a temperature of 160–170° for 9 hours and then raised to 190° for a few minutes. Residue, pale yellow.

Found : Loss in weight, 6.6%.

In both cases residue increased in weight on standing almost regaining original weight. These reactions correspond most closely to



Between 190 and 200° C., decomposition was active, ethylene-diamine is expelled and the residue became grey and black. The evolution continued up to 250°, when if the residue was now heated under a small flame decrepitation occurred.

The Action of Heat on $[\text{Pt}(\text{NH}_3)_4](\text{HF}_2)_2$.

At 150° C. for 1 hour, acid gas evolved and crystals lost clear appearance.

Found : Loss in weight, 10.0%.

At 140–150° C. and then temperature raised rapidly to 195° C. Residue started to blacken.

Found : Loss in weight, 10.1%.

Loss of 2 moles of hydrofluoric acid requires 11.7%.

Residue leached with water and crystallised by the addition of acetone.

Found : Pt, 58.9%.

Calculated for $\text{Pt}(\text{NH}_3)_4\text{F}_2 \cdot 1.5\text{H}_2\text{O}$; Pt, 59.45%.

At 140–150° C. until all hydrofluoric acid is expelled and then raised slowly to 170–180° C. the evolution of some NH_3 was detected ; residue straw coloured.

Found : Loss in weight, 12.1%.

If the residue was now cautiously and quickly heated over a free flame, further evolution of NH_3 could be detected in the initial decomposition. Above 200° C., total decomposition started evolving dense white pungent fumes, with acid reaction ; black residue.

The Action of Heat on $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4](\text{HF}_2)_2 \cdot 0.5\text{H}_2\text{O}$.

At 100° C. the odour of pyridine was faint. At 130° C. a pale yellow colour was spreading throughout the mass. At 185–190° C. the substance melted to a dark brown liquid ; strong odour of pyridine followed by pungent acid fumes. Reaction appeared to cease after about 1 hour, when the substance solidified to a dark amber vitreous mass.

Found : Loss in weight, 25%.

Calculated : Loss for $2\text{HF} + 0.5\text{H}_2\text{O}$, 8.2% ; loss for $2\text{HF} + 0.5\text{H}_2\text{O} + 2\text{C}_5\text{H}_5\text{N}$, 34.6%.

The residue was soluble in water, giving a dark amber solution. Preliminary investigations have indicated that the solution contains a compound in which $\text{Pt} : \text{C}_5\text{H}_5\text{N} : \text{F} = 1 : 2 : 2$. The compound is being investigated further and the results will be reported later.

The Action of Heat on $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2 \cdot 9\text{H}_2\text{O}$.

This substance readily loses $6\text{H}_2\text{O}$ over P_2O_5 (Plowman, *loc. cit.*). However, due to the rapidity with which the trihydrate takes up H_2O the 9-hydrate was used as a starting product.

(1) At 110° for 2 hours, odour of pyridine, and the residue was yellow and hygroscopic.

(2) At 140° for a further 2 hours, odour of pyridine and the residue was dark brown and hygroscopic.

Found : (1) Loss in weight, 24% (110°C.) ; (2) loss in weight, 36% (140°C.).

Calculated : Loss for $9\text{H}_2\text{O}$, 22.8% ; loss for $9\text{H}_2\text{O}$ and $2\text{C}_5\text{H}_5\text{N}$, 45% ; loss for $6\text{H}_2\text{O}$ and $2\text{C}_5\text{H}_5\text{N}$, 37.4%.

SUMMARY.

The decomposition on heating of the fluorides and hydrogen fluorides of $[\text{Pt}(\text{NH}_3)_4]^{++}$, $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]^{++}$, and $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]^{++}$ has been described. The hydrogen fluorides decompose in a characteristic manner depending on the nature of the coordinating addenda attached to the platinum atom. With $[\text{Pt}(\text{NH}_3)_4]\text{F}_2$ the temperature at which ammonia is lost and that at which total decomposition occurs are too close to effect a possible preparation of a diammine compound. However the compounds of $[\text{Pt}(\text{C}_5\text{H}_5)_4]^{++}$ show evidence of decomposing to compounds of the dipyridine series.

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STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART III. OXIDATION OF THE TETRAMMINE PLATINUM II FLUORIDES.

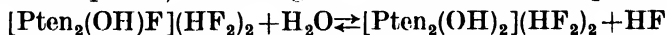
By R. A. PLOWMAN, B.Sc., A.S.T.C. (Chem.).

Manuscript received, March 7, 1950. Read, April 5, 1950.

In a previous communication (Plowman, 1949) the preparation of the fluorides and hydrogen fluorides of the tetrammine platinum II type were described. This communication reports the preparation of some platinum IV compounds by oxidation of the corresponding platinum II types with hydrogen peroxide.

The compounds $[\text{Pt}(\text{NH}_3)_4]\text{F}_2$ and $[\text{Pt}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\text{F}_2$ were oxidised readily with hydrogen peroxide yielding the corresponding dihydroxo compounds, $[\text{Pt}_4(\text{NH}_3)_4(\text{OH})_2]\text{F}_2 \cdot 0.5\text{H}_2\text{O}$ and $[\text{Pt}_4\text{en}_2(\text{OH})_2]\text{F}_2 \cdot 3\text{H}_2\text{O}$ as well defined, colourless, crystalline substances soluble in water. Salts of the $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]^{++}$ ion have previously been described (Mellor, 1937), but as far as is known the fluoride has not previously been characterised. Compounds of the analogous ion $[\text{Pten}_2(\text{OH})_2]^{++}$ do not appear to have been reported. Further investigation is being carried out on the reactions of this ion and the results will be reported in a separate communication.

When the above oxidations were carried out in the presence of concentrated hydrofluoric acid, the ethylene diamine compound yielded $[\text{Pten}_2(\text{OH})\text{F}](\text{HF}_2)_2$ as a colourless crystalline compound, readily soluble in water. Oxidation of the $[\text{Pt}(\text{NH}_3)_4]^{++}$ ion in the presence of concentrated hydrofluoric acid yielded $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2](\text{HF}_2)_2$ crystallising in colourless prisms, soluble in water. The analytical results on this compound gave fluorine percentages that were slightly high (ca. 2-3%), whereas experience has shown that with a pure compound the fluorine percentage is usually low (ca. 2-3%). This may be indicative of the simultaneous formation of a compound analogous to that obtained with the ethylenediamine compound, viz. $[\text{Pt}(\text{NH}_3)_4(\text{OH})\text{F}](\text{HF}_2)_2$. When an aqueous hydrofluoric acid solution of $[\text{Pten}_2(\text{OH})\text{F}](\text{HF}_2)_2$ was evaporated to complete dryness at the temperature of the water bath the residue approximated in composition to $[\text{Pten}_2(\text{OH})_2](\text{HF}_2)_2$. Solution of this residue in hydrofluoric acid (48%) and precipitation with acetone yielded a substance approximating to the original compound, indicating the existence of the equilibrium



The oxidation of $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]\text{F}_2$ with H_2O_2 was not successful. The oxidation of the $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]^{++}$ ion with H_2O_2 was made the subject of a separate project, and preliminary investigations indicate that this ion is not oxidised with hydrogen peroxide. The results of these investigations will be reported in a later communication.

EXPERIMENTAL.

All reactions involving fluorides were carried out in platinum vessels.

(1) *Dihydroxo bis (ethylenediamine) Platinum IV fluoride 0.5-Hydrate and 3-Hydrate.*

$[\text{Pt}^{\text{II}}\{\text{C}_2\text{H}_4(\text{NH}_2)_2\}_2]\text{F}_2 \cdot 2\text{H}_2\text{O}$ (Plowman, *loc. cit.*), 1.5 g., in 10-15 ml. of H_2O oxidised with 2 ml. of 30% H_2O_2 . The solution was concentrated to 1 ml. on the water bath and on the addition of methanol-ether, (1) was precipitated as the 3-hydrate in agglomerates of small, colourless

crystals, very soluble in water, insoluble in acetone, alcohol and ether. Yield, 1.46 g. = 86%. Over P_2O_5 , 2.5 moles of H_2O were lost, forming the 0.5 hydrate. The 2.5 moles of H_2O were regained on exposure to air.

Found (compound dried over P_2O_5): Pt, 49.1%; F, 9.3%; H_2O (increase in weight on exposure to air), 11.3%.

Calculated for $[Pt^{IV}\{C_2H_4(NH_2)_2\}_2(OH)_2]F_2 \cdot 0.5H_2O$: Pt, 49.2%; F, 9.6%; increase for 2.5 H_2O , 11.4%.

(2) *Dihydroxo tetrammine Platinum IV fluoride, 0.5 Hydrate.*

$[Pt^{II}(NH_3)_4]F_2 \cdot 1.5H_2O$ (Plowman, *loc. cit.*) 1.5 g. in 10–15 ml. H_2O oxidised with 2 ml. of 30% H_2O_2 . The solution was repeatedly evaporated on the water bath until excess H_2O_2 expelled. Crystallisation occurred on evaporation and was completed by the addition of acetone. Yield, 1.56 g. = 98% of (2) as clear colourless prisms soluble in water, insoluble in acetone, alcohol, and ether. The compound commenced to decompose about 230° C. with simultaneous loss of NH_3 and HF.

Found: Pt, 57.0%, 56.8%; F, 10.6%.

Calculated for $[Pt^{IV}(NH_3)_4(OH)_2]F_2 \cdot 0.5H_2O$: Pt, 56.7%; F, 11.0%.

(2) dissolved in cold H_2O yielded a sparingly soluble sulphate with sodium sulphate.

Found (material recrystallised from hot H_2O and dried over P_2O_5): Pt, 49.3%; S, 8.3%.

Calculated for $[Pt(NH_3)_4(OH)_2]SO_4$: Pt, 49.6%; S, 8.14%.

(3) *Dihydroxo tetrammine Platinum IV hydrogen fluoride.*

$[Pt^{II}(NH_3)_4]F_2 \cdot 1.5H_2O$ (Plowman, *loc. cit.*) dissolved in 2–3 ml. HF (48%) and the solution oxidised by the addition of 3–4 ml. 30% H_2O_2 . After evaporation $[Pt^{IV}(NH_3)_4(OH)_2](HF_2)_2$ crystallised in clusters of small jagged colourless prisms, with an acid reaction on litmus paper. Yield, 2.06 g. Dried at 100° C. and finally over P_2O_5 . Deliquescent.

Found: Pt, 52.4%; F, 21.0%.

Dissolved in 3–4 mls. concentrated HF and recrystallised by the addition of acetone.

Found: Pt, 51.7%; F, 20.8%.

Calculated for $[Pt^{IV}(NH_3)_4(OH)_2](HF_2)_2$: Pt, 52.0%; F, 20.3%.

At 150° C. the compound lost HF, the loss being accompanied by some decomposition (slight blackening).

Found: 2 hours at 150–160° C., lost 14.4%.

Calculated loss for 2 moles HF: 10.7%.

(4) *Fluoro hydroxo bis (ethylenediamine) Platinum IV hydrogen fluoride.*

$[Pt^{II}\{C_2H_4(NH_2)_2\}_2]Cl_2$, 2.1 g., in 10–15 ml. H_2O was treated with excess of freshly prepared Ag_2O . To the filtrate excess HF was added and the solution evaporated to dryness on the water bath. The residue, dissolved in 3–5 ml. of HF (48%), was oxidised with 1.0 ml. H_2O_2 (30%). A few seconds after the addition of H_2O_2 a vigorous (almost violent) effervescence of gas occurred and the temperature of the solution rose markedly. After evaporation on the water bath to incipient crystallisation, crystallisation of the soluble compound was completed by the addition of acetone. Washed with acetone and finally with ether. Yield, 1.76 g. of micro crystals colourless and slightly deliquescent after drying over P_2O_5 . The compound gave an acid reaction with moist litmus paper.

Found (compound dried over P_2O_5): Pt, 45.7%, 45.0%; F, 21.5%.

Calculated for $[Pt\{C_2H_4(NH_2)_2\}_2(OH)F](HF_2)_2$: Pt, 45.5%; F, 22.1%.

Dissolved in concentrated HF and recrystallised in two fractions by the addition of acetone.

Found (on first fraction): F, 21.9%; (on second fraction): F, 21.1%.

In a separate preparation, the solution after oxidation was evaporated to dryness on the water bath and finally dried in the oven at 100–105° C.

Found : Pt, 45.6% ; F, 18.6%.

Calculated for $[\text{Pt}(\text{C}_2\text{H}_4(\text{NH}_2)_2(\text{OH})_2)(\text{HF}_2)_2]$: Pt, 45.7% ; F, 17.8%.

Dissolved in 2–3 ml. HF (48%) and crystallised by the addition of acetone.

Found : Pt, 45.7% ; F, 20.3%.

At 120° C. the compound commenced to lose HF, and at 150–160° C. there was a steady evolution of HF.

Found : 2 hours at 150–160° C., 4.9% loss ; further 20 minutes at 165–180° C. (decomp.), 7.5% loss.

Calculated loss of 1 mole of HF : 4.7%.

The residue was deliquescent.

SUMMARY.

The preparation of some complex platinum IV fluorides and hydrogen fluorides has been described. These are $[\text{Pt}(\text{NH}_3)_2(\text{OH})_2]\text{F}_2 \cdot 0.5$ and $3\text{H}_2\text{O}$; $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2]\text{F}_2 \cdot 0.5\text{H}_2\text{O}$; $[\text{Pt}(\text{NH}_3)_4(\text{OH})_2](\text{HF}_2)_2$; and $[\text{Pt}(\text{NH}_3)_2(\text{OH})\text{F}](\text{HF}_2)_2$. All were prepared from the corresponding platinum II compound by oxidation with H_2O_2 . They are well defined, colourless crystalline compounds. The $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_4]^{++}$ ion was not oxidised with the same experimental conditions.

ACKNOWLEDGEMENT.

The author wishes to thank Dr. F. P. J. Dwyer for his interest and guidance during the course of this work.

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OCCULTATIONS OBSERVED AT SYDNEY OBSERVATORY DURING 1949.

By W. H. ROBERTSON, B.Sc.

(Communicated by the GOVERNMENT ASTRONOMER.)

Manuscript received, February 9, 1950. Read, April 5, 1950.

The following observations of occultations were made at Sydney Observatory with the 11½-inch telescope. A tapping key was used to record the times on a chronograph, with the exception of number 195, which was an eye and ear observation. No correction was applied to the recorded times, either for personal effect or to allow for error in the Moon's tabular longitude. The reduction elements were computed by the methods given in the Occultation Supplement to the Nautical Almanac for 1938 and the reduction completed by the method given there. The necessary data were taken from the Nautical Almanac for 1949, the Moon's right ascension and declination (hourly table) and parallax (semi-diurnal table) being interpolated therefrom.

Table I gives the observational material. The serial numbers follow on from those of the previous report (Robertson, 1949). The observers were H. W. Wood (W) and W. H. Robertson (R). In all cases the phase observed was disappearance at the dark limb. Table II gives the results of the reductions which were carried out in duplicate. The N.Z.C. numbers given are those of the Catalog of 3539 Zodiacal Stars for the Equinox 1950·0 (Robertson, 1940), as recorded in the Nautical Almanac.

TABLE I.

| Serial No. | N.Z.C. No. | Mag. | Date. | U.T. | Observer. |
|------------|------------|------|---------|------------|-----------|
| | | | | h m s | |
| 187 | 647 | 5·5 | Jan. 11 | 13 32 56·4 | R |
| 188 | 797 | 6·3 | Jan. 12 | 12 29 44·7 | R |
| 189 | 771 | 6·1 | Apr. 4 | 9 35 30·1 | R |
| 190 | 1365 | 6·1 | Apr. 8 | 11 37 22·8 | R |
| 191 | 1684 | 7·0 | May 8 | 11 31 29·4 | W |
| 192 | 1373 | 6·1 | June 29 | 7 34 49·5 | R |
| 193 | 2063 | 6·7 | Aug. 1 | 13 05 19·4 | W |
| 194 | 2317 | 6·6 | Aug. 3 | 8 35 10·3 | R |
| 195 | 2468 | 6·9 | Aug. 4 | 9 47 33·0 | W |
| 196 | 2644 | 6·3 | Aug. 5 | 12 14 38·3 | W |
| 197 | 2270 | 5·4 | Aug. 30 | 8 19 20·8 | W |
| 198 | 2583 | 5·8 | Sept. 1 | 9 10 13·6 | W |
| 199 | 3197 | 6·5 | Nov. 26 | 12 22 32·3 | W |
| 200 | 545 | 4·2 | Dec. 4 | 9 39 46·8 | W |
| 201 | 552 | 3·0 | Dec. 4 | 10 26 41·3 | W |

TABLE II.

| Serial No. | Luna- tion. | p | q | p^2 | pq | q^2 | $\Delta\sigma$ | $p\Delta\sigma$ | $q\Delta\sigma$ | Coefficient of | |
|------------|----------------|-----|-----|-------|-----|-------|----------------|-----------------|-----------------|----------------|----------------|
| | | | | | | | | | | $\Delta\alpha$ | $\Delta\delta$ |
| 187 | 322 | +52 | +85 | 27 | +44 | 73 | -1.3 | -0.7 | -1.1 | + 4.0 | +0.95 |
| 188 | 322 | +85 | +53 | 72 | +45 | 28 | -2.4 | -2.0 | -1.3 | +10.2 | +0.64 |
| 189 | 325 | +92 | +39 | 85 | +36 | 15 | -1.4 | -1.3 | -0.5 | +11.2 | +0.52 |
| 190 | 325 | +34 | -94 | 12 | -32 | 88 | -2.8 | -1.0 | +2.6 | + 0.1 | -1.00 |
| 191 | 326 | +89 | -45 | 80 | -40 | 20 | -1.0 | -0.9 | +0.4 | + 8.6 | -0.82 |
| 192 | 328 | +66 | -75 | 44 | -50 | 56 | -0.8 | -0.5 | +0.6 | + 5.3 | -0.92 |
| 193 | 329 | +69 | -73 | 47 | -50 | 53 | -0.4 | -0.3 | +0.3 | + 4.9 | -0.94 |
| 194 | 329 | +96 | -28 | 92 | -27 | 8 | -0.6 | -0.6 | +0.2 | +11.7 | -0.52 |
| 195 | 329 | +68 | +73 | 47 | +50 | 53 | -2.5 | -1.7 | -1.8 | +10.4 | +0.63 |
| 196 | 329 | +83 | -56 | 69 | -46 | 31 | -0.4 | -0.3 | +0.2 | +11.0 | -0.56 |
| 197 | 330 | +80 | -60 | 64 | -48 | 36 | +0.4 | +0.3 | -0.2 | + 8.3 | -0.80 |
| 198 | 330 | +68 | +73 | 47 | +50 | 53 | -1.2 | -0.8 | -0.9 | + 9.3 | +0.71 |
| 199 | 333 | +81 | -58 | 66 | -47 | 34 | -0.6 | -0.5 | +0.3 | +13.9 | -0.22 |
| 200 | 333 | +97 | -23 | 95 | -22 | 5 | -1.7 | -1.6 | +0.4 | +13.6 | +0.06 |
| 201 | 333 | +98 | -22 | 95 | -22 | 5 | -2.0 | -2.0 | +0.4 | +13.6 | +0.07 |

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THE GEOLOGY OF THE CANOWINDRA DISTRICT, N.S.W.

PART II. THE CANOWINDRA-COWRA-WOODSTOCK AREA.

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With Plate I and one text-figure.

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- II. Physiography.
- III. Palæozoic Strata.
- IV. Structure—
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 - Faults—
 - The Southern Continuation of the Columbine Mountain Fault Zone.
 - Other Faults.
- V. Intrusive Rocks—
 - The Garnetiferous Porphyry.
 - The Cowra Granodiorite.
 - Minor Intrusions.
- VI. Summary and Acknowledgements.

I. INTRODUCTION.

The area considered lies immediately to the south of the district described in Part I of this series (Stevens, 1948).

Previous geological literature concerning the district is confined to brief notes (chiefly on mineral deposits) in some of the Annual Reports of the N.S.W. Department of Mines ; a report on the limestones near Canomodine and Walli (Carne and Jones, 1919), and reports on dam sites on the Belubula River (Kenny, 1941 ; Mulholland, 1946). The latest regional map (1945) indicates the presence of Lower Palæozoic and Devonian strata, invaded by granite, but the area had not been previously mapped in detail.

The present paper is an attempt to explain the structure and stratigraphy of the region, and to correlate it with that of the Cargo district. Detailed accounts of the intrusive rocks will be reserved for later publications.

II. PHYSIOGRAPHY.

Two main streams drain the district—the Lachlan and Belubula Rivers. They follow meandering east-west courses in valleys about 1,000 feet above sea level, and join some distance to the west of the area considered. The divide between them runs roughly east-west, and is generally 500–700 feet higher.

The Belubula River has cut steep-sided, and sometimes vertical, gorges through the more resistant rocks (e.g. Silurian tuffs and cherts, and Devonian quartzites and conglomerates). In these places the physiography is relatively youthful ; elsewhere the country is more mature, especially where the river flows through porphyry near Canowindra.

Outcrops are generally poor near the Lachlan-Belubula divide, but become better as the Belubula River is approached. The highest point in the area is Malongulli Trigonometrical Station (The Sugarloaf), 2,109 feet above sea level. It is not situated on the divide between the rivers, but owes its prominence to the superior resistance of its quartzite capping. The quartzites of the Conimbla Ranges and the granodiorite ridge between Cowra and Canowindra also form marked physiographic features.

III. PALÆOZOIC STRATA.

Ordovician.

Sedimentary rocks of Upper Ordovician age occur as narrow inliers between Malongulli Trig. Station and Woodstock. They are elongated north-south and are bounded on their western margin by a fault.

The rock types are mainly fine-grained sandstones and quartzites, some of which have a slaty cleavage. The following graptolites were collected by Mr. K. Sharp and the author (locality—one mile north of Woodstock, 810305*):

- Diplograptus calcaratus* var. *vulgatus*.
- Diplograptus rugosus* var. *apiculatus*.
- Dicellograptus forchammeri* var. *flexuosus*.
- Dicellograptus angulatus*.
- Dicellograptus* cf. *caduceus*.
- Climacograptus bicornis*.
- Climacograptus tubiliferus*.
- Climacograptus* cf. *minimus*.

Most of these rocks are in the zone of *Dicranograptus clingani* (the lower part of the Caradocian of Britain).

Silurian.

The Silurian rocks of the Cargo district extend south across the Belubula River towards Woodstock and Cowra. Slates, tuffs, cherts, limestones and occasional quartzites and conglomerates are the main rock types, and these are invaded by a garnet-bearing porphyry and the Cowra granodiorite. The andesites and tuffs east of Woodstock and Walli are also thought to be of Silurian age, equivalent to the Andesitic Series of Cargo. Thus, they would be the oldest of the Silurian system in the district.

The series consists of andesites of several types, interstratified with tuffs and breccias (as at Woodstock), slates and cherts. North-east of Woodstock, the andesites have large, closely-packed felspar phenocrysts. They are occasionally amygdaloidal as well, like those east of Canomodine Creek, Cargo. Quartz-epidote veins and traces of copper minerals are again characteristic of this series; and in this district several barytes deposits (Raggatt, 1925) are associated with the andesites. Succeeding beds cannot be observed in this area because of faulting.

In the "Cranky Rock" area, fine-grained crystal tuffs overlie the Canomodine limestone. The tuffs are interbedded with, and grade into, cherts and slates. South-east of "Mountain View", a high hill is composed of a conglomerate consisting of andesite pebbles. A similar rock has been noted on the east side of Liscombe Pools Creek (801472). Strata which include red to chocolate-coloured shales are adjacent to the garnetiferous porphyry south of "Cranky Rock". They have been noted in many other localities, both in this district and to the north, at approximately the same stratigraphical horizon.

* Six-figure numbers are grid co-ordinates on the one-inch military maps, Canowindra and Cowra. See also map (Plate I).

Next in the sequence is the garnetiferous porphyry, most of which appears to be a sill-like intrusive. It is generally conformable, though locally transgressive.

Slates, tuffs and some quartzites overlie the porphyry to the west. Some of the tuffs resemble the porphyry in hand-specimen, but the fragments are usually smaller and more closely packed than the phenocrysts of the porphyry. No large feldspars occur in the tuffs, which appear to have a greater percentage of quartz in them.

East and south of "Mountain View" the strata are mainly slates (buff, greenish and red), with some tuffs and thin limestone beds. One limestone bed occurs at intervals along the west side of the porphyry belt of Liscombe Pools Creek, and another on the eastern side. Fossils found north-west of Woodstock (762350) and near "Malongulli" gate (788473) include *Tryplasma*, *Halysites*, *Favosites* and brachiopods. *Halysites*, *Favosites* and bryozoa occur in a limestone lens surrounded by porphyry and tuff on Liscombe Pools Creek (798470). These limestones and the associated strata are younger than the Canomodine limestone, and possibly younger than most of the tuffs which overlie it. (See text-figure.)

Correlation with the Cargo-Toogong District.

The first paper of this series (Stevens, 1948) expresses some doubt about the stratigraphical position of the Canomodine limestone. Although very similar to the parallel Cargo Creek belt, it seemed to occur at a higher horizon, separated from the Cargo Creek limestone by tuffs and slates. On following the Canomodine limestone south, it was found to be overlain by tuffs similar to those overlying the Cargo Creek limestone to the north. Comparison of the sequence on the Belubula River with that between the two limestones south of Cargo suggests that the Canomodine and Cargo Creek limestones are equivalent, and that the andesites and tuffs of Barrajin Trig. Station are equivalent to the Cargo Andesitic Series (see Table I).

TABLE I.

Comparison of the Silurian Sequences. (A) at the South-eastern End of the Canomodine Limestone, (B) in the Cargo Creek Area.

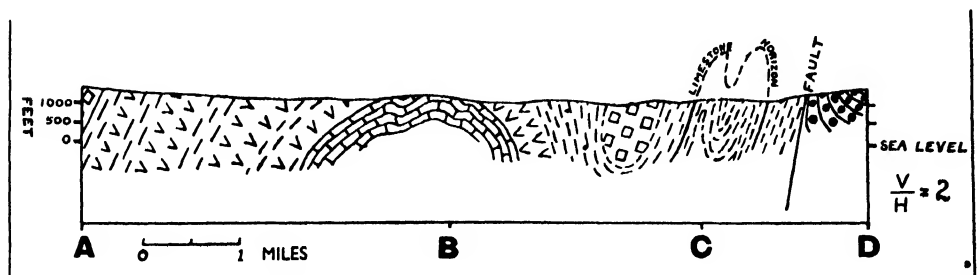
| Sequence A. | Sequence B. |
|--|----------------------------|
| | Canomodine limestone. |
| | ? Fault? |
| 4. Garnetiferous porphyry. | 4. Garnetiferous porphyry. |
| 3. Slates and cherts. | 3. Slates and cherts. |
| 2. Canomodine limestone. | 2. Cargo Creek limestone. |
| 1. Barrajin Trig. andesites and tuffs. | 1. Cargo Andesitic Series. |

Upper Devonian.

Western Area. The Upper Devonian rocks of the Mandagery Range and Nangar Mountains (Stevens, 1948) continue south along the western boundary of the area mapped beyond the Cowra-Grenfell Road.

In the Mandagery Range, quartzites are the dominant rock type, but further south the proportion of interbedded shales and grits increases, giving rise to less rugged country, especially where the Lachlan and Belubula Rivers have cut through the series. As early as 1878, Wilkinson recognised Devonian rocks west of Canowindra, but the southern extension of this series is shown on all previous maps as Silurian. Wilkinson records *Lepidodendron*, *Sigillaria* and a "small bivalve shell" from these rocks.

Eastern Area. The Upper Devonian rocks of the Black Rock Range do not continue far south of the Belubula River, as they are cut off by a fault. An outlier of quartzite occurs east of the main belt, and on it Malongulli Trig. Station is situated.



The oldest beds are quartzites showing evidence of shallow water deposition in the form of ripple-marks and rain-prints. Etheridge (1909) records *Lepidodendron*, *Lingula gregaria* and fish-plates from these rocks. Some thin beds of reddish shales occur within the quartzite series. Conglomerates follow, and these are overlain by red shales and green mudstones with plant remains.

IV. STRUCTURE.

Folding of the Palæozoic Strata.

Ordovician. Owing to the poor outcrops, the structure of the Ordovician rocks is uncertain, but from exposures one mile north of Woodstock it is probable that the folding is closer than in the Silurian and that an unconformity exists between them.

Silurian. Although the amplitude of the folds in the Silurian is much greater than in the Ordovician, the intensity of folding in the former series increases from west to east, as the major fault zone is approached. Angles of dip steepen, become vertical and the strata overturn on the margins of the porphyry upstream from "Cranky Rock". Angles of dip are also very steep at the porphyry boundary on the Canowindra-Cargo Road; in the headwaters of Binni Creek, and at the northern margin of the Cowra granodiorite.

The most striking major fold is the Cranky Rock plunging anticline, first noted by Kenny (1941) in an unpublished report on the Cranky Rock damsite. The structure in the Canomodine limestone is difficult to determine because of its massive nature, strong cleavage (N. 20° W.), and lack of fossil bands. It is possible that several minor folds exist within the limestone, as some have been observed south, and on the flanks, of the main outcrop. The most convincing proof of the fold is seen further south, where slates, tuffs and cherts dip gently under the porphyry, and the beds outcrop in a broad arc; the fold plunging gently south.

The garnetiferous porphyry follows the strike of the beds except in the "nose" of the fold. The irregularity in outcrop here suggests a fault, but it may be due to a local transgression of the bedding planes.

South of the Cranky Rock anticline, another anticline emerges to the east of Tenandra Creek. It appears to plunge north, as the porphyry margin curves around, together with a change in strike. Minor synclines occur on the eastern flanks of both anticlines.

To the east, near Liscombe Pools Creek, all dips are either to the west or vertical, except for one near the major fault on the Belubula River. Overfolding is likely in this area, and both folds and faults suggest pressure from the west.

Upper Devonian.

Western Area. Except near the Conimbla Mountains, the Upper Devonian strata have not been followed far across their strike, but it is known that all the rocks dip west on their eastern margin. A synclinal structure has been noted west of Canowindra (Wilkinson, 1878).

The strike varies from N. 30° E. at Nyranng Creek to N. 30° W. north-west of Cowra. The dip varies from 18° to 90°. An anticline and south-plunging syncline are present between Conimbla Mountain and the Lachlan River; this structure shows up well on aerial photographs, as the rock types are interbedded grits, quartzites and shales.

Eastern Area. The synclinal structure of the Upper Devonian in the Black Rock Range is cut off to the south by the southern continuation of the Columbine Mountain fault, and the narrow strip of Upper Devonian west of Malongulli Trig. Station dips steeply to the west. The outlier itself is in the form of a syncline with gentle dips; almost a horizontal capping.

Faults.*The Southern Continuation of the Columbine Mountain Fault Zone.*

North of the Belubula River the Columbine Mountain fault is joined by a fault from the north-west, and for several miles south the fault can be traced along the boundary of Silurian and Devonian rocks, the latter appearing to dip under the former. The Upper Devonian rocks are nearly vertical near the fault, and there is ample evidence of brecciation and shearing.

South of the point where the Upper Devonian rocks disappear Ordovician strata occur east of the main fault, and due to lack of outcrops the evidence of faulting is not as well defined. The main evidence for a fault along the western margin of the Ordovician north of Walli lies in the contiguity of strata high in the Silurian sequence and Ordovician rocks. However, some outcrops of iron and manganese ore (due to deposition along fault planes) occur along this boundary, as well as in the Ordovician strata.

Further south, the position of the fault is hidden by soil cover, but has been tentatively placed along the Ordovician-Silurian slate boundary. One mile north of Woodstock an outcrop of manganese ore occurs at the boundary of Ordovician sandy slate and Silurian sheared andesites. Faulting is clearly indicated.

Other Faults.

Two transecting faults have been noted east of Canowindra, where quartzite and slate beds have been displaced. A continuation of this line of faulting may be represented to the south-west by a zone of shearing in the porphyry and tuffs.

Minor faults displace a limestone lens and tuff beds near "Malongulli" gate, and signs of faulting occur between that locality and the head of Emu Creek.

The steep and sometimes vertical dip of the Upper Devonian quartzites along their eastern margin south-west of Canowindra suggests some faulting, and it is further exemplified by displacement of beds W.N.W. of Cowra.

Consideration of the stratigraphy of the area between Cargo and the Belubula River demands that, if the Cargo Creek and Canomodine limestones are equivalent, either a fault exists along the north-east margin of the Canomodine limestone or that an overfolded syncline occurs between the two beds.

V. INTRUSIVE ROCKS.

The Garnetiferous Porphyry.

The garnet-bearing porphyry previously seen near Toogong and Cargo continues south, and is well-developed near Canowindra. The rock is fairly uniform in appearance, except in shear zones. Idiomorphic phenocrysts of altered plagioclase and biotite, and corroded quartz, are present in a fine-grained groundmass.

The porphyry mass is mainly concordant, but tongues transgress the bedding planes of the associated sediments. It is noteworthy that the porphyry is restricted to the upper part of the Silurian, and has not been found invading the Andesitic Series or the Upper Devonian rocks. Where the porphyry outcrops strongly, large, rounded tors result; these are more pointed and elongated where the rock has suffered shearing.

Certain phases exhibit a clastic nature under the microscope; but this seems to be due to brecciation of an intrusive rock rather than evidence of a pyroclastic origin. In many places the porphyry is intrusive into tuffs of a similar mineralogical composition, and mapping of boundaries between the two rock types is difficult.

Similar porphyries and tuffs extend south through Boorowa to Yass, where three horizons of tuffs and similar intrusive porphyries have been recognised (Brown, 1940).

The Cowra Granodiorite.

This intrusion has a north-south elongation and is nearly conformable with the Silurian sediments, which dip towards it on the eastern side. It is intrusive into these sediments, which have suffered only slight metamorphism. On the western side, it is adjacent to the garnetiferous porphyry, but field relations are obscured by soil cover.

In hand specimen the rock is fairly uniform throughout the mass except for a narrow marginal phase (on the eastern side), which is a type of granite-porphyry. The usual type of Cowra granodiorite is a mottled black and white, phanocrystalline rock with clear vitreous quartz, dull white feldspars and idiomorphic lustrous biotite. Red garnet is frequently present, often in or near the margins of xenoliths. The latter are abundant, especially near the southern end of the intrusion. Most of them have been completely recrystallised, but some retain the banding of the original sediment.

Nothing is known of the age of the intrusion beyond the fact that it is post-Silurian. It does not show any gneissic banding or marked orientation of minerals, so it is probably younger than Late Silurian and is possibly of Kanimblan age (Browne, 1929).

Minor Intrusions.

Most of the minor intrusions of the district occur near the major fault zone through Walli and Woodstock. The largest of these invades Ordovician strata south of Malongulli Trig. Station. The main rock type is a pyroxene lamprophyre, which weathers readily to a greenish-brown soil. This mass is intersected by dykes of a peculiar red rock consisting of perthite, green pyroxene, zeolites and quartz, with magnetite and apatite.

Further north, dykes of a finer-grained rock of similar mineralogical composition invade Silurian slates. It is considered that all these minor intrusions are related to one another, and to the granophyres and monzonite-porphyries of the Cargo district.

VI. SUMMARY AND ACKNOWLEDGEMENTS.

Ordovician, Silurian and Upper Devonian strata have been folded into plunging anticlines and synclines as in the Cargo district, of which the area considered is the southern extension.

The Columbine Mountain fault zone has been traced south towards Woodstock and an account is given of the faulted area between Walli and the Belubula River.

It has been shown that the garnetiferous porphyry, though locally intrusive, is mainly conformable with the Silurian sediments, and has been folded with them.

Introductory notes on the Cowra granodiorite are given, showing that it is an elongated, sill-like intrusion, almost conformable with the Silurian strata.

The writer wishes to acknowledge financial assistance from a Commonwealth research grant; also, some of the work was done during the tenure of a Deas-Thomson scholarship in Geology at Sydney University.

Thanks are due to those members of staff of the Geology Department, Sydney University, who have given me assistance; also to Mrs. K. Sherrard, for determining the graptolites. The writer wishes to thank Mr. K. R. Sharp, Mr. G. Packham and other students for their help in the field; Mr. and Mrs. Whatmore of "Malongulli", and Mr. and Mrs. W. Ridout of Walli for their hospitality.

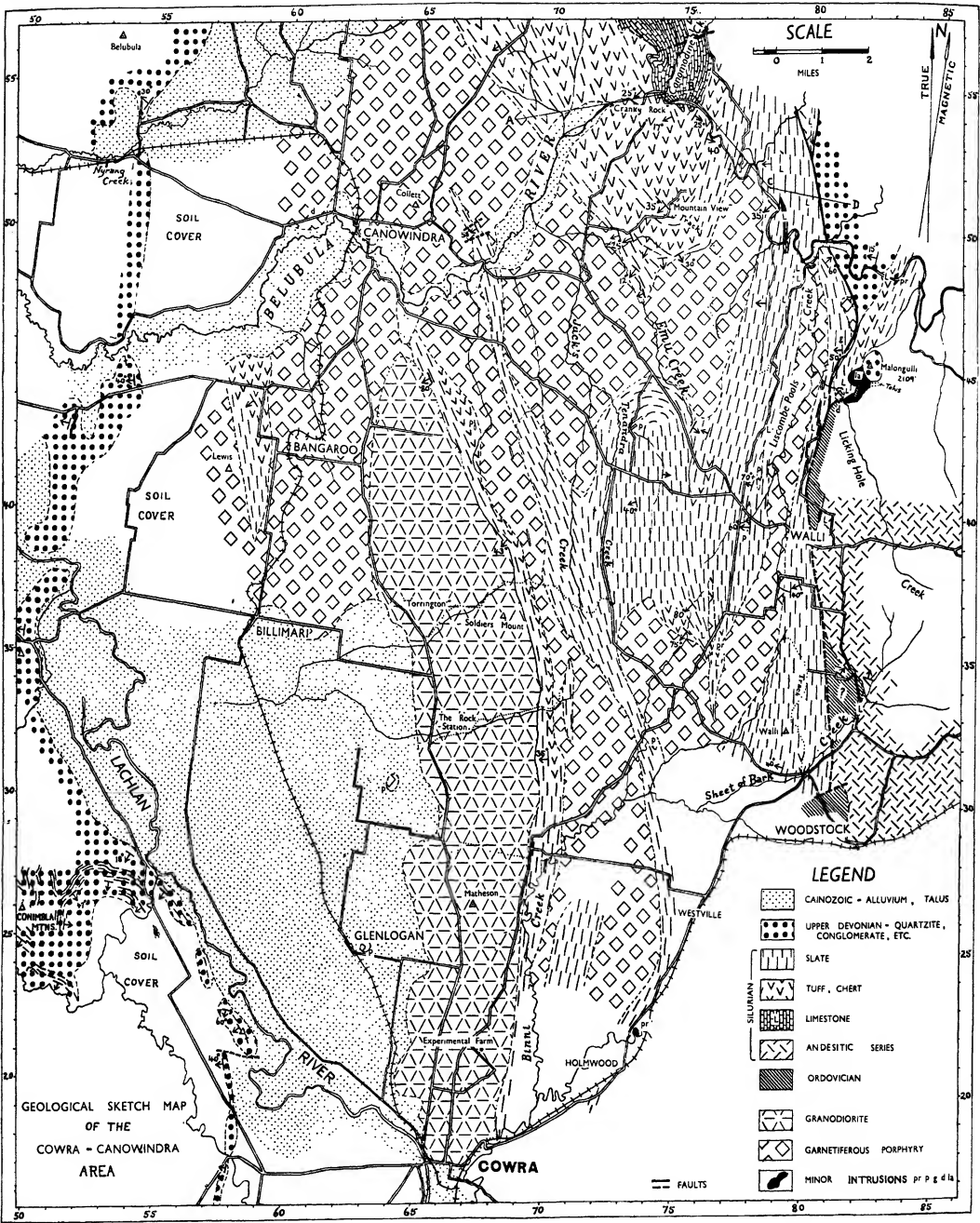
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EXPLANATION OF PLATE.

PLATE I.

Geological sketch map of the Cowra-Canowindra area. Letters *pr*, *p*, *g*, *d*, *la* refer to minor intrusions related to porphyryite, garnetiferous porphyry, granophyre, dolerite and lamprophyre respectively.



THE FIVE PROPERTIES CONCERNED IN THE TRANSPORT OF THE ACTIVE CORRODANT AGENT.

By R. C. L. BOSWORTH, Ph.D., D.Sc.

Manuscript received, March 27, 1950. Read, May 3, 1950.

THE PROPERTIES INVOLVED IN DETERMINING THE RATE OF CORROSION.

An analysis of the process of the corrosive loss of matter in the simple case of a metal dissolving in a corrodant liquid without complications due to such phenomena as pitting, dezincification or of bimetallic corrosion, has been recorded in the three earlier papers of this series (Bosworth, 1949). The analysis revealed that for a given metal, in a given corrodant and at a given temperature, there are five properties concerned in determining the rate. These five properties, with the symbols suggested for them in parentheses, are :

- (a) the maximum corrosion rate (q_0),
- (b) the conductance term (j),
- (c) the compliance term (K),
- (d) the inertial term (ξ), and
- (e) the electrochemical driving force (E).

The quantity q_0 is the rate at which the corrosion process will proceed, under the given conditions of temperature and pH, when the necessary depolarizing agent is made instantly available wherever required. The quantity j is a measure of the effective driving force change with ease of accessibility to the surface. K is a measure of the change of driving force with quantity of metal corroded by unit volume of the corrodant and ξ is a measure of that property which tends to maintain the reaction by maintaining the convective flow of corrodant to the surface under attack once the reaction is proceeding at a steady rate. ξ may be identified with an inertial (or inductive) term following the claim by the author (Bosworth, 1946) that natural thermal convection currents bestow an inductive character on the process of heat flow. ξ then is a property which indicates the magnitude of the opposition which the reaction offers to any change in rate.

The analysis in the earlier papers gave the product of the two properties K and E , viz. KE , but was not sufficiently complete to enable the two properties to be separated. More recently, however (Bosworth, 1949a), the magnitude of E for some of the systems studied has been obtained by polarization measurements so that for these systems it is possible to derive all five of the physical properties concerned in determining the rate of corrosion.

For example, for copper in 30 % aqueous acetic acid at 20° C. we have, from overvoltage measurements,

$$E=0.70 \text{ volt.}$$

Previous measurements have given for this system

$$KE=1.20 \text{ mgrms. litres}^{-1},$$

so that

$$K=1.72 \text{ mgrms. litres}^{-1} \text{ volts}^{-1}.$$

Again, for copper in 60/40 acetic acid/acetic anhydride

$$E=1.10 \text{ volts}$$

$$KE=2.3 \text{ mgrms. litres}^{-1},$$

so that

$$K=2.09 \text{ mgrms. litres}^{-1} \text{ volts}^{-1}.$$

The other properties applying to these systems have all been recorded in the earlier papers (Bosworth, 1949), so that now a complete list can be given. Of these properties the value of K —the compliance term—and certain functions derived from K are of particular interest. Prominent among these derived properties are those having zero dimensions and those with the dimension of time.

THE MAGNITUDE OF THE COMPLIANCE TERM.

The property K is a measure of the change in concentration of dissolved metal required to produce a unit change in the corrosion cell e.m.f. E . Mathematically

$$K = \frac{\partial C_m}{\partial E} \dots\dots\dots (1)$$

where C_m is the concentration of the dissolved metal.

The variation of an electrode potential with the concentration C_c of the ion concerned in the electrode reaction is given by the Nernst equation :

$$E = E_0 + \frac{RT}{nF} \ln C_c$$

where R is the gas constant, F the faraday and n the valence of the ion.

At 20° C. this takes the value

$$E = E_0 + \frac{0.0248}{n} \ln C_c$$

$$\text{or } \frac{\partial C_c}{\partial E} = 40.3nC_c \dots\dots\dots (2)$$

Since the concentration of the dissolved metal C_m is connected by some stoichiometric relation with the concentration C_c of the ion concerned in determining the corrosion cell e.m.f., such as

$$dC_m = \lambda dC_c,$$

equation (1) may be transcribed to the form

$$K = 40.3\lambda nC_c \dots\dots\dots (3)$$

where λ is the ratio of the equivalent weight of the dissolving metal to the equivalent weight of the ion concerned in determining the corrosion cell e.m.f.

From the magnitude of K derived above we may thus obtain figures for the quantity λnC_c . These figures are :

For copper in 50% aqueous acetic acid = 0.043 milligrammes per litre.

For copper in 60/40 acetic acid/anhydride = 0.052 milligrammes per litre.

Since λn is not expected to be greatly different from unity, we conclude that the concentration of the ion responsible for controlling the corrosion cell e.m.f. is of the order of 0.05 milligramme per litre. This particular fact may be used to eliminate certain mechanisms which might otherwise be postulated in explanation of the corrosion reaction. Thus the active depolarizing agent

cannot be copper ions in solution as the concentration of these ions is indeterminate in a fresh acid and much greater than 0.05 milligramme per litre in used acid. Again the concentration of hydrogen ions even in the non-aqueous solutions is many thousands of times greater than 0.05 milligramme per litre, so that the hydrogen ions cannot be effective corroding agent. This leaves dissolved oxygen as the only other obvious corroding agent. The concentration of dissolved oxygen in a saturated solution of acetic acid at 20° C. is about 0.2 milligramme per litre. It is not unreasonable to expect that the somewhat lesser figures of 0.05 might represent at least the order of the magnitude of the concentration of the dissolved oxygen in the vicinity of the surface undergoing corrosive attack.

From these considerations on the magnitude of the compliance term (K) we are thus lead to the conclusion that it is, most probably, the dissolved oxygen in solution which is responsible for the chemical rate controlling step in the corrosion process, and that, as this oxygen is used up by the corrosion process, the effective corrosion cell e.m.f. is progressively changed by a factor determined by the quantity K . The fact that the supply of an oxidizing agent is necessary for the maintenance of the corrosion of copper by organic acids has, of course, long been known on thermochemical grounds, and it is at least noteworthy that a purely physical analysis of the flow processes involved leads to the same conclusion.

DIMENSIONLESS QUANTITIES DERIVED FROM THE COMPLIANCE TERM.

In problems involving heat flow in fluid systems the dimensionless ratio known as the Prandtl number (Pr) has assumed great importance. Pr is the ratio of the diffusion constant for momentum, or kinematic viscosity (η/ρ) to the thermal diffusivity or thermometric conductivity ($k/C_p\rho$). The analogous properties in the transport process involving the conveyance of the active depolarizing agent is the ratio of the kinematic viscosity to the diffusivity of the depolarizing agent (D_c).

Let us use the symbol Pc for this dimensionless quantity—the analogue of the Prandtl number in corrosion problems. .

We have

$$Pc = \frac{\eta}{\rho D_c} = \frac{\eta K E}{\rho j} \dots\dots\dots (4)$$

All the properties concerned in equation (4) for the various systems studied have been measured and we have for

| | | |
|--|-------|-----------|
| Copper in 30% aqueous acetic acid | | $Pc=1.90$ |
| Copper in 60/40 acetic acid/anhydride | | $Pc=1.96$ |
| Steel " " " " | | $Pc=1.86$ |
| Brass " " " " | | $Pc=2.16$ |
| Phosphor bronze in 60/40 acetic acid/anhydride | | $Pc=2.08$ |

The relative constancy of the values of this property is perhaps significant and would appear to indicate that the transport of momentum and of the depolarizing agents in these corrodant liquids is effected by a similar molecular mechanism.

Another dimensionless quantity involving K is the expression

$$\frac{d^3 g \xi K^2 E^2}{\eta j (1 - q/q_0)}$$

which, as we have seen in the third paper of this series, plays a part in the corrosion reaction analogous to that played by the Grashof group in the natural convection of heat. Let us consider the possible variation of this

quantity with change in temperature. ξ , as we have seen, is the larger the lower the density of the original corrodant and thus is expected to increase slightly with increase in temperature. The quantity K , depending as it does on the solubility of a gas in a liquid, will decrease rapidly with temperature increase. E will, in general, change but slightly with temperature. The quantity j/KE , identified as a diffusion coefficient, and the viscosity will both change rapidly with temperature following an exponential-reciprocal relationship. Thus Barrer (1943) has written

$$\eta = \text{Const } e^{E_A/RT} \dots\dots\dots (3)$$

$$D = \text{Const } e^{-E_A/RT} \dots\dots\dots (4)$$

Identifying j/KE with D_c , the diffusion coefficient for the active corroding agent we find that the quantity j/KE is independent of temperature unless the two activation energies of equations (3) and (4) are different. Accordingly we expect that the temperature variation of

$$\frac{d^3 g \xi K^2 E^2}{j(1-q/q_0)}$$

will be largely dominated by the change in K and the quantity will thus assume lower values at higher temperatures. We have seen, however, that at low values of

$$\frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}$$

the quantity

$$\frac{qd}{j(1-q/q_0)}$$

will become practically a constant; or, except for values of q approximating to q_0 , the product qd is expected to be practically constant, or the rate of loss of matter from small cylindrical bodies by corrosion at high temperatures under quiescent conditions is expected to be proportional to the length rather than to the area. This particular phenomenon has already been noted in the third paper of this series in connection with the corrosion of copper cylinders at 70% C.

TRANSIENTS IN CORROSION PHENOMENA.

We have seen that the flow of matter in corrosion phenomena involves resistive, inductive and capacitative elements. Accordingly it is to be expected that the corrosion process will show transient phenomena. It is, of course, fairly common knowledge that the initial rate of corrosion may differ widely from that attained in the same system after the lapse of time (Speller, 1935). It now appears that we have, in some simple cases, a method of estimating the "time constant" for the corrosion process by analogy with what amounts to an equivalent electric circuit. In the systems which have so far been studied in this series the intensity of the convection current as estimated by the magnitude of the dimensionless quantity

$$\frac{d^3 g \xi K^2 E^2}{\eta j(1-q/q_0)}$$

is relatively small and we may, as a first approximation, disregard the inductive element and estimate the time constant in terms of the resistance and the capacity.

Let us consider an area A under corrosion attack. Let V be the volume of the corrodant. The corrosion rate q is now given by

$$\frac{1}{q} = \frac{1}{q_0} + \frac{V}{Aj}$$

The corrosion cell e.m.f. (E) thus drives a mass current qA , or

$$\frac{q_0 j A^2}{j A + q_0 V}$$

so that the resistance term (R) is given by

$$R = \frac{(j A + q_0 V) E}{q_0 j A^2}, \quad \dots\dots\dots (5)$$

The capacity term (C) is likewise given by

$$C = VK, \quad \dots\dots\dots (6)$$

and the time constant (τ) by

$$\tau = RC = \frac{KEV^2}{jA^2} \left(1 + \frac{jA}{q_0 V}\right) \quad \dots\dots\dots (7)$$

$$= \frac{V^2}{D_c A^2} \left(1 + \frac{jA}{q_0 V}\right) \quad \dots\dots\dots (8)$$

The ratio $\frac{V}{A}$ is equal to the depth of the layer of corrodant over the surface,

while j/q_0 is the measure of the intercept of the $\frac{1}{q}$ versus z line on the axis, or

a measure of the effective resistance of all factors concerned in determining the rate of corrosion other than those involving cathodic polarization, the measure being expressed in terms of the equivalent thickness (δ) of the quiescent layer of the corrodant. Equation (8) may thus be written

$$\tau = \frac{z^2}{D_c} \left(1 + \frac{\delta}{z}\right) \quad \dots\dots\dots (8)$$

Expressions of a similar type for the resistance capacity time constants of transport processes hold for all diffusional systems (Bosworth, 1949*b*). Since values of D_c have been found for the various systems studied figures may be found for different geometrical configurations. For $1/D_c$ we may take 200 sec. cms. as a representative figure. For a metal covered to a depth of 1 cm. the time constant is therefore of the order

400 seconds or 6.3 minutes.

For a surface covered to a depth of 2 cms. this becomes

1200 seconds or 20 minutes.

and one covered by 10 cms.

22,000 seconds or 360 minutes.

The time constant, while varying roughly as the square of the depth of corrodant covering the surface under attack, is for any system of laboratory dimensions, small in comparison with a day and experimental determinations of the loss of weight over periods of five days or more should therefore not be subject to significant errors arising from the initial condition of unsteady state corrosion.

SUMMARY.

Corrosion of a metal by a corrodant liquid which attacks the surface uniformly is controlled by five physical properties: (a) the maximum rate, (b) a conductance term, (c) a compliance term, (d) an inertial term, and (f) the electrochemical driving force. All five factors may be determined by methods outlined in the previous papers.

In the case of copper in acetic acid the magnitude of the compliance term is shown to be dependent on the solubility of the corrodant for oxygen.

The rate of corrosion of a specimen freshly placed in a corrodant is expected to show transient phenomena, and where the contribution of the inertial element may be neglected the time constant for such transients is roughly proportional to the square on the depth of immersion of the specimen.

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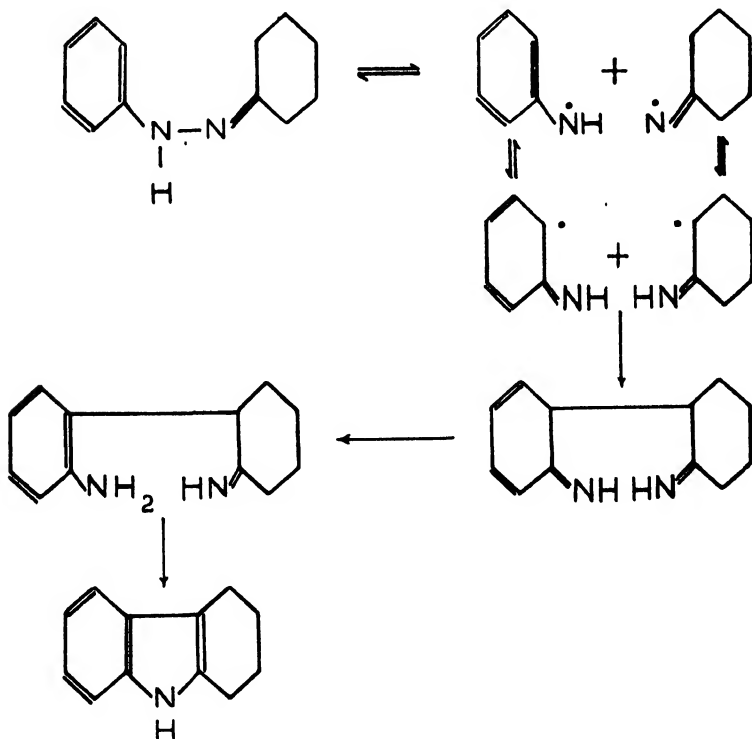
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THE MECHANISM OF THE FISCHER INDOLE SYNTHESIS.

By P. H. GORE,
G. K. HUGHES
and E. RITCHIE.

Manuscript received, April 11, 1950. Read, May 3, 1950.

The mechanism suggested by Robinson and Robinson (1918, 1924) for the Fischer indole synthesis has been accepted as a satisfactory working hypothesis for many years. Consequently the theory of Pausacker and Schubert (1949*a*, 1949*b*) that the reaction proceeds by the free radical mechanism summarised below for the case of *cyclohexanone phenylhydrazone*, required careful consideration.

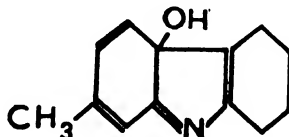


Evidence along four lines was adduced in favour of this mechanism.

(a) It was found that a mixture of equal weights of *cyclohexanone o*-tolylhydrazone and 2-methyl-*cyclohexanone* phenylhydrazone on cyclisation by glacial acetic acid gave 11-methyl- and 8,11-dimethyl-tetrahydrocarbazolenines and after dehydrogenation of the neutral fraction, carbazole and 1-methyl-carbazole. These four products were formed in nearly equivalent proportions. (It may be remarked here that a fifth product, 1,8-dimethyl-carbazole, also would be expected in small amount according to both theories.)

From this result it was concluded that the Fischer indole synthesis is an intermolecular reaction and that homolytic fission of the N-N linkage occurs.

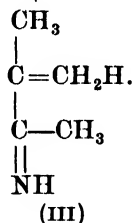
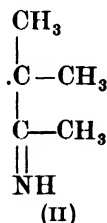
(b) From the cyclisation of *cyclohexanone* 2-chloro-5-methyl-phenylhydrazone by dilute sulphuric acid, Pausacker and Robinson (1947) isolated not only the expected product, 8-chloro-5-methyl-tetrahydrocarbazole but also a small amount of a second substance to which the structure (I), with the name 12-hydroxy-7-methyl-1,2,3,4-tetrahydroisocarbazole given later (Barnes, Pausacker and Schubert, 1949) was assigned. Other substances of this type were subsequently obtained (Barnes, Pausacker and Schubert, *loc. cit.*).



(I)

It was claimed that the hydrolysis of the *o*-halogen in the substituted phenylhydrazones could be readily explained by the free radical mechanism.

(c) The well-known facile cyclisation of methyl isopropyl ketone phenylhydrazones may be explained, since the intermediate free radical (II) would be stabilised by hyperconjugation as in (III).



(d) The corresponding primary arylamines were produced in small amounts in the cyclisation of the phenylhydrazones, *o*-methoxyphenylhydrazones, *o*-tolylhydrazones and *o*-chloro-phenylhydrazones of *cyclohexanone* (Barnes, Pausacker and Schubert, *loc. cit.* ; Pausacker and Schubert, *loc. cit.* (b)).

These facts were explained by the equation $\text{ArNH} + \dot{\text{H}} \rightarrow \text{ArNH}_2$.

However it can be shown clearly (1) that all of the evidence cited above can be satisfactorily interpreted without recourse to a free radical mechanism and (2) that there is convincing evidence that the cyclisation does not involve free radicals.

(a) These results may be very simply explained by hydrolysis of the hydrazones and recombination of the two hydrazines with the two ketones (or hydrazone interchange without the participation of water) to form four hydrazones, including *cyclohexanone* phenylhydrazones and 2-methyl-*cyclohexanone* *o*-tolylhydrazones, not initially present, followed by intramolecular cyclisation. While the experiments described below were in progress this same explanation was suggested by Robinson and its possibility admitted by Pausacker (1949 ; Pausacker and Schubert, *loc. cit.*), who then found that the cyclisation of *cyclohexanone* *o*-tolylhydrazones in the presence of phenylhydrazine by glacial acetic acid gave a product from which carbazole could be isolated after dehydrogenation.

It has been known for many years that hydrazone interchange can occur (e.g. Freer, 1899; Frank and Phillips, 1949; for a beautiful example of the related case of semicarbazones, see Conant and Bartlett, 1932), and additional examples pertinent to the question of the mechanism of cyclisation have now been found. The experimental results may be summarised as follows:

(1) Acetone phenylhydrazone (1 mol.) and *cyclohexanone* (1 mol.) boiled in glacial acetic acid for half an hour gave a 50% yield of tetrahydrocarbazole.

(2) Phenylhydrazine (1.2 mol.) and *cyclohexanone* 2,4-dinitrophenylhydrazone (1 mol.) refluxed in glacial acetic acid for 24 hours gave an 18% yield of tetrahydrocarbazole and a 25% yield of 2,4-dinitrophenylhydrazine.

(3) *Cyclohexanone* 2,4-dinitrophenylhydrazone (1 mol.) and acetone phenylhydrazone (5.3 mol.) refluxed in glacial acetic acid for 32 hours gave a 16% yield of tetrahydrocarbazole.

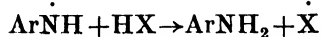
(4) Benzaldehyde phenylhydrazone (1 mol.) and *cyclohexanone* (1 mol.) boiled in glacial acetic acid for 25 hours gave a 5% yield of tetrahydrocarbazole.

Now in the proposed free radical mechanism the radicals $C_6H_5\dot{N}H$ and $C_6H_{10}\dot{N}$ would be very reactive since they would not be stabilised by a large amount of resonance energy. Once formed, they would rapidly react further and it is unlikely that they would recombine to an appreciable extent. Hence according to this mechanism the critical step in determining whether a given hydrazone will cyclise is the formation of free radicals. Under the conditions used in the above experiments neither acetone phenylhydrazone nor *cyclohexanone* 2,4-dinitrophenylhydrazone cyclises. Therefore the formation of tetrahydrocarbazole in each of the experiments and the isolation of 2,4-dinitrophenylhydrazine in experiment (2) must result from a hydrazone interchange and renders unnecessary the postulation of a free radical mechanism.

(b) This argument is valueless. The structures of the so-called tetrahydroisocarbazoles are uncertain and even if they had the structures assigned to them it would still remain to be proved that they are formed from intermediates involved in the normal cyclisation. Moreover it is by no means apparent how the hydrolysis of the *o*-halogen in a substituted phenylhydrazone can be explained by the free radical mechanism.

(c) The ready formation of indolenines and carbazolenines is to be expected on the Robinsons' theory also. It is well known that carbonium ions with the formal positive charge on a tertiary carbon atom are formed more readily than those with the charge on a secondary carbon atom.

(d) If free arylimino radicals were formed then by analogy with the behaviour of other free radicals (Waters, 1946) they would be expected to react mainly with the solvent thus:



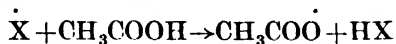
leading to the production of large, not small amounts of the primary arylamine. It is well known that phenylhydrazine can function both as an oxidising and reducing agent and it has also been found that by refluxing acetone phenylhydrazone with dilute sulphuric acid aniline is produced in small yield, even though cyclisation does not occur. Therefore the formation of primary arylamines is satisfactorily explained by oxidation-reduction. In support of this contention may be cited the fact that the cyclisation of *cyclohexanone* 2,4,6-tribromophenylhydrazone gives comparatively high yields of 2,4,6-tribromoaniline and 1,3,5-tribromobenzene (Barnes, Pausacker and Schubert, *loc. cit.*), Chattaway and Irving (1931) having shown that 2,4,6-trichlorophenylhydrazine is readily oxidised to 1,3,5-trichlorobenzene.

Three further arguments against the free radical mechanism can be put forward.

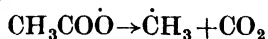
(e) Free radical reactions in solution are generally far from "clean" and usually do not give high yields (Waters, *loc. cit.*). By careful working a yield of over 95% of tetrahydrocarbazole can be obtained by the glacial acetic acid cyclisation of *cyclohexanone phenylhydrazone*.

(f) Free phenylimino radicals would surely combine to give at least a trace of hydrazobenzene, which under the prevailing acid conditions would rearrange to benzidine. Tests which detect 0.00003 g. of benzidine gave negative results when applied to the appropriate fraction from the cyclisation of 39.5 g. of *cyclohexanone phenylhydrazone*.

(g) Free radicals in glacial acetic acid solution would be expected to react extensively with the solvent mainly by the reaction



which would be followed by



and hence large amounts of carbon dioxide should be liberated. In a typical experiment the yield of carbon dioxide was only 0.4% mol./mol. of hydrazone. Moreover, it was found that when acetone phenylhydrazone was refluxed with acetic acid carbon dioxide was slowly evolved. This means that part of the carbon dioxide in the previous experiment was produced by a reaction not connected with cyclisation. The remainder may have arisen from some free radical reaction but in view of the very small amounts involved it is believed that its production is unrelated to the cyclisation. Tentatively it is suggested that it may be produced by thermal decomposition of the acetic acid, since much of it is evolved rapidly during the short strongly exothermic cyclisation reaction. It is thought that there may be present isolated points of high energy content resulting in the rupture of the acetic acid molecule before the energy can be otherwise dissipated.

EXPERIMENTAL.

Products were identified by m.p. and mixed m.p. with authentic specimens.

Formation of Tetrahydrocarbazole.

(1) A solution of acetone phenylhydrazone (4.1 g.; 1 mol.) and *cyclohexanone* (2.7 g.; 1 mol.) in glacial acetic acid (25 ml.) was refluxed for half an hour and then cooled. Tetrahydrocarbazole (2.3 g.; 50%) m.p. 116–7° C. separated, and more was undoubtedly present in the mother liquor since it is moderately soluble in glacial acetic acid.

(2) A solution of *cyclohexanone* 2,4-dinitrophenylhydrazone (5 g.; 1 mol.) and phenylhydrazine (2 g.; 1.2 mol.) in glacial acetic acid (35 ml.) was refluxed for 24 hours (not continuously). The dark solution was diluted with water and then shaken with an equal volume of ether, which took up the resinous material that had precipitated. After a few minutes orange crystals began to separate from the ether extract. The material (2.3 g.; m.p. 184–92° C.) which was collected after 18 hours was a mixture of *cyclohexanone* 2,4-dinitrophenylhydrazone and 2,4-dinitrophenylhydrazine. The latter substance was obtained in pure form (0.9 g.; 25%) by three crystallisations from alcohol.

The ether mother liquor was washed with dilute acid and evaporated to dryness. The residue on steam distillation (600 ml. of distillate) afforded tetrahydrocarbazole (0.55 g.; 18%).

(3) Acetone phenylhydrazone (18.4 g.; 5.3 mol.) and *cyclohexanone* 2,4-dinitrophenylhydrazone (6.5 g.; 1 mol.) in glacial acetic acid (45 ml.) were refluxed for 32 hours and then steam distilled. From the distillate 2,000 ml., after acidifying with hydrochloric acid, tetrahydrocarbazole (0.65 g.; 16%) was obtained.

(4) A solution of benzaldehyde phenylhydrazone (2.4 g.; 1 mol.) and *cyclohexanone* (1.2 g.; 1 mol.) in glacial acetic acid (45 ml.) was refluxed for 25 hours, and then steam-distilled. Tetrahydrocarbazole (0.1 g.; 5%) was collected from the distillate (800 ml.).

Action of Dilute Sulphuric Acid on Acetone Phenylhydrazone.

The conditions were those used by Barnes, Pausacker and Schubert (*loc. cit.*). Pure acetone phenylhydrazone (24.2 g.) free from aniline, was refluxed with water (65 ml.) and concentrated sulphuric acid (7.2 ml.) for half an hour. After cooling, the reaction mixture was extracted with ether, which on evaporation left unchanged acetone phenylhydrazone (4.0 g., 16%). The aqueous layer was made strongly alkaline and extracted with ether, the extract dried and the ether removed. The residue was then fractionated under reduced pressure, the first few drops only being collected. From this distillate aniline (0.36 g.; 2.4%) was isolated through its hydrochloride and further identified through its 5-bromosalicylidene derivative. The residue in the flask contained phenylhydrazine (about 4.5 g.; 29%), determined by oxidation with Fehling's solution, which does not attack acetone phenylhydrazone.

Cyclisation of Cyclohexanone Phenylhydrazone.

Glacial acetic acid (190 ml.) was refluxed vigorously for 15 minutes in a stream of carbon dioxide-free nitrogen, then cooled and cyclohexanone phenylhydrazone (39.5 g.) added. Traces of carbon dioxide were swept out, then the issuing gases passed through several gas wash-bottles containing barium hydroxide solution and the acetic acid solution carefully brought to its boiling point. At the moment of vigorous reaction carbon dioxide was evolved. When the reaction had subsided refluxing was continued for half an hour. The barium carbonate (0.17 g.; i.e. 0.4% mol. of CO_2 /mol. of hydrazone) was collected, washed and dried. The reaction mixture on cooling deposited tetrahydrocarbazole (26.8 g.) and a second crop (8.2 g.; total 98%) was obtained by evaporating the mother liquor to half bulk and carefully adding water.

The second mother liquor was basified and shaken with an ethereal solution of the total tetrahydrocarbazole. The brownish yellow extract was washed with water and then shaken with dilute sulphuric acid (3×50 ml. of 3.2 N) when a slight amorphous brown precipitate (< 0.01 g.) formed at the interface. Neither this precipitate nor any of the acid extracts gave a positive test for benzidine with potassium dichromate or ferrieyanide or carbon disulphide-bromine water.

Action of Glacial Acetic Acid on Acetone Phenylhydrazone.

When acetone phenylhydrazone (18 g.) was refluxed in glacial acetic acid (195 ml.) in a stream of pure nitrogen as above, barium carbonate (0.12 g.; 0.5%) was gradually precipitated during 2½ hours.

ACKNOWLEDGEMENT.

This work was carried out during the tenure of a Dunlop Research Scholarship held by one of us (P.H.G.).

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THE PERMIAN ROCKS OF THE MANNING-MACLEAY PROVINCE, NEW SOUTH WALES.

By ALAN H. VOISEY, D.Sc.

With Plate II.

Manuscript received, February 20, 1950. Read, May 3, 1950.

INTRODUCTION.

In this paper is presented an account of the Permian rocks outcropping in the region embraced by the valleys of the Manning, Camden Haven, Hastings and Macleay rivers which will be called the Manning-Macleay Province. Details of a number of sections have been published in a series of papers dealing with smaller areas, but an attempt is now made to correlate the various beds throughout the whole province.

For reference purposes and in order to show the occurrences of the major units on a map it is suggested that the Macleay Series (Voisey, 1934), which probably corresponds to the Lower Marine Series of the Hunter Valley, may be divided into three stages as follows :

Warbro Stage, consisting of micaceous mudstones with small proportions of tuff, sandstone, shale, limestone and conglomerate, with a maximum measured thickness of 1,640 feet ;

Yessabah Stage, comprising calcareous sediments (including the Yessabah crinoidal limestone) and being very fossiliferous, with maximum thickness of 1,260 feet ; and

Tait's Creek Stage, consisting of chocolate and grey shales, sandstones and conglomerates with a maximum thickness of 500 feet.

This division, based on the lithology, is somewhat arbitrary and it is not suggested that a detailed correlation with Osborne's stages in the Hunter Valley should be made. There are, however, a number of similarities between some of the sediments and the faunas which indicate that the two sequences are of the same general age.

In a preliminary account of part of the province (Voisey, 1934) the name "Kempsey Series" was given to the sedimentary strata around Kempsey. Because of the paucity of outcrops subsequent evidence of age has only been obtained in one place, a quarry beside the Kempsey-Telegraph Point road, where marine Carboniferous shells were discovered. However, this information, together with Professor L. A. Cotton's discovery of *Rhacopteris* beside the same road, and lithological resemblances of some of the rocks to those in known sections, indicates that most, if not all, of the area shown as "Kempsey Series" on the map (Voisey, 1934, Plate XVI) should now be regarded as Carboniferous and not Permian as previously suggested. On the accompanying map (Plate II), therefore, a possible fault separating Carboniferous and Permian beds is shown running north-west from Kundabung.

MACLEAY SERIES.

Geographical Distribution.

The distribution of the three stages of the Macleay Series is shown on the map (Plate II). No occurrences are known north of the Kempsey Area Fault

and none south of the Manning River Fault System. The chocolate or purple shales of the Tait's Creek Stage are revealed in road cuttings between Moparrabah and Yessabah but further south they are inconspicuous. The crinoidal limestone of the Yessabah Stage may be picked up at intervals beyond Dondingalong as far as the old lime kilns near Kundabung. Since outcrops become fewer to the south, the mapping of the continuation of the Permian beds is conjectural, being based on the topography and the soil.

The limestone and its associates reappear some miles to the south-west of Wauchope (Voisey, 1939*b*, 259). Together with Carboniferous strata they are unconformably overlain by the Triassic sediments of the Lorne Basin, which form the Broken Bago Range.

Limestone is recorded from a place five miles west of the village of Comboyne, on the eastern side of a small tributary of Karagnine Creek, which flows into the Ellenborough River. Carne and Jones (1919, 271) state that it is traceable for some distance down the gorge. This belt continues southward to the neighbourhood of Wingham and Taree (Voisey, 1938 ; 1939*c*).

Numerous isolated Permian outcrops have been mapped in the Kimbriki-Mount George area, where they are separated from each other by the fractures of the Manning River Fault System (Voisey, 1939*a* ; 1939*c*).

Structural Relations.

The remains of the Permian deposits are preserved only in sunken areas within a large fault-girt block, which has been depressed relatively to its surroundings.

North of the Kempsey Area Fault Lower Palæozoic slates and phyllites appear, all Upper Palæozoic sediments having been removed by erosion. Similarly to the south, Devonian rocks are in contact with Permian and Carboniferous strata, demonstrating a smaller but still important movement.

Within this main down-thrown block the Macleay Series outcrops along the eastern limb of the Parrabel Anticline (Voisey, 1934) in synclines and small faulted blocks.

A critical examination of each locality where a section has been measured shows that only lower Permian rocks are present, and nowhere have the equivalents of the Coal Measures or Upper Marine Series been recognised. The question as to whether a much thicker Permian sequence ever existed over the area must remain open.

The existence of the Triassic strata of the Lorne Basin (Voisey, 1939*b*) lying with a relatively gentle dip on the upturned edges of Permian and Carboniferous strata suggests that there was quite a long break between the onset of the Upper Palæozoic orogeny and the formation of the freshwater lake. It may be, therefore, that the early orogenic movements which caused the folding of the older sediments took place a considerable time before the close of the Permian period. As indicated in earlier papers (Voisey, 1939*b*, 254 ; 1939*c*, 406) the larger faults, the Kempsey Area fault and Manning River Fault system, occurred late in the orogeny and were responsible for the lowering of the block of already folded Upper Palæozoic sediments between them. The Triassic lake formed in the depressed area perhaps a short time afterwards.

Stratigraphy.

Difficulties have been met in the field in the separation of the Kullatine Series and the Tait's Creek Stage of the Macleay Series since the Kullatine tillites in places weather to a chocolate or reddish colour not unlike that of the overlying shales (Voisey, 1936, 185). The calcareous matrix of the shales containing glaciated pebbles at Yessabah and the marine fossils indicate that these beds are related closely to the Macleay Series. In fact, the uppermost

shales are interbedded with the limestones of the Yessabah Stage and these also have a pink and sometimes purple colour. So close is the relation in this locality that the separation of the Tait's Creek and Yessabah Stages has to be quite arbitrary. This point is emphasised because W. R. Browne has now placed the Lochinvar shales in the Kuttung Series of the Carboniferous (Osborne, 1949, 207), and the Tait's Creek shales have been compared with these (Woolnough, 1911, 164).

Tait's Creek Stage. The Tait's Creek Stage is taken to include all beds above the Carboniferous Kullatine Series and below the Fenestellidæ Mudstone horizon (Voisey, 1934, 339).

There is a great variation in the nature of the sediments in this stage. Between Willi Willi and Yessabah they are largely chocolate and grey shales making up about 200 feet of the sequence, followed by 40 feet of green tuff. The shales contain a number of pebbles, some glaciated.

At Dondingalong sandstones form the basal unit but contain two lenticular bands of "shell conglomerate".

In the Manning District tuffs and tuffaceous sandstones close to the base of the series also include a "shell conglomerate" of similar character containing marine fossils, including *Spirifer* and *Aviculopecten*. This rock appears in portions 117 and 118, parish of Taree, and portion 118, parish of Wingham near Western's Quarry. At Kimbriki and Mount George tuffs and banded mudstones are several hundred feet in thickness and directly overlie the Carboniferous tillites and tuffs.

Yessabah Stage. The division between this and the underlying Tait's Creek Stage is in each section placed where there is a definite increase in the amount of calcareous material. This seems to occur at approximately the same point throughout the province and represents some big change in the conditions of sedimentation. In contrast with the underlying Stage, the Yessabah Stage shows little lithological or faunal variation over an area representing probably 3,000 square miles of sea floor.

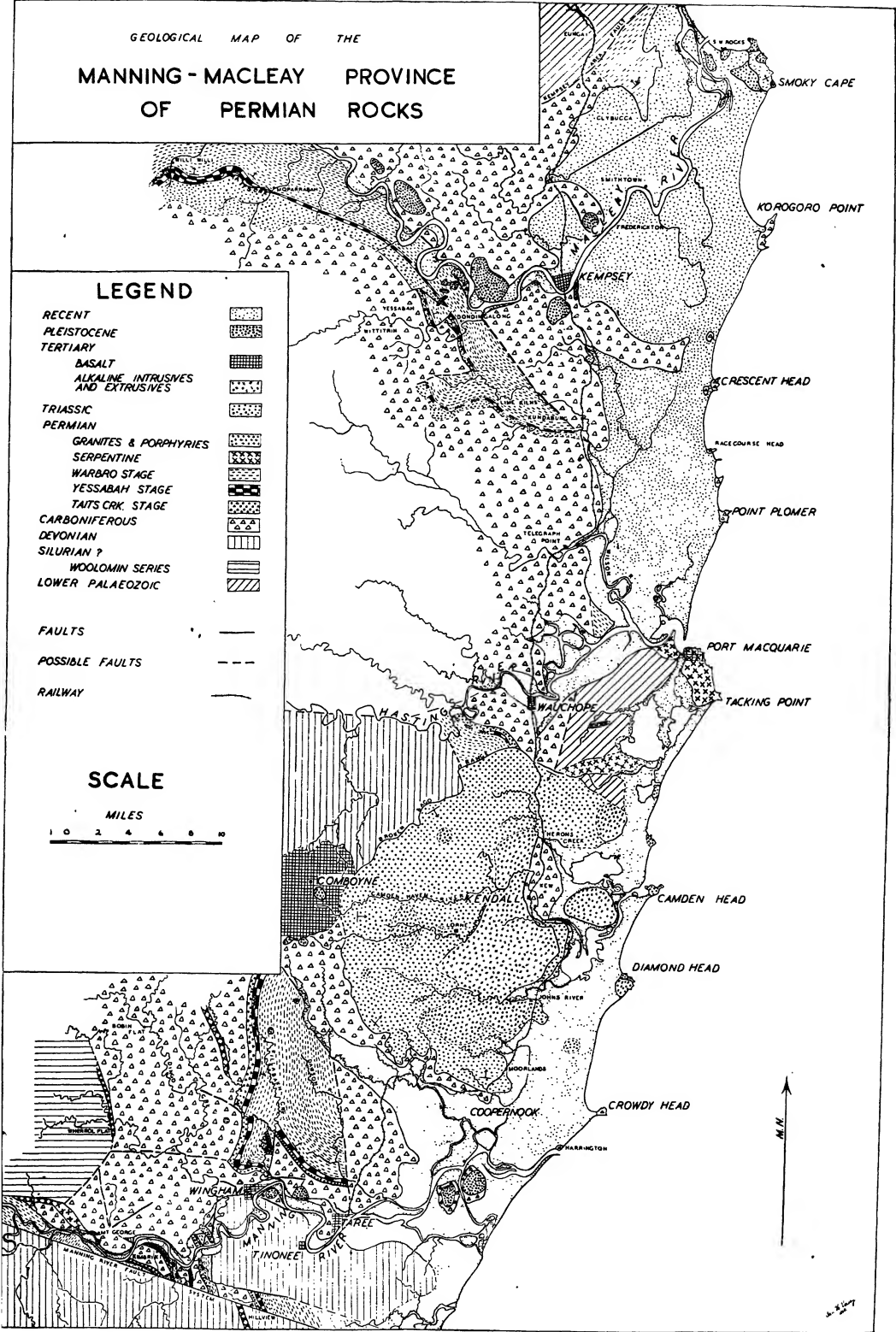
The Fenestellidæ Mudstones, which are generally well developed throughout the province, pass upwards and in some places laterally into limestones. The overlying Yessabah limestone has been used for the mapping of the whole province. Its upper and lower limits vary slightly from place to place, usually at the expense of the mudstones. The rock is coarsely crystalline and has been described as a marble. Fossils are well preserved in spite of the texture. The limestone varies somewhat in colour, usually being pink and purple in the north and grey to bluish-grey in the south. Towards Kimbriki it passes into a dark tuffaceous limestone losing much of its crystalline character.

The topmost unit of the Yessabah Stage is usually limestone, partly silicified, which weathers to a spongy mass of silicified fossil remains. Where *Cladochonus nicholsoni* is abundant, as at Willi Willi, macaroni-like masses occur.

Warbro Stage. A distinct change in lithology from limestones to micaceous mudstones and tuffs is recognisable in most localities. There is generally a sudden break in slope stratigraphically above the silicified limestone, the Warbro Stage sediments forming the lower ground.

Owing to the softness of the mudstones outcrops are infrequent, among the best being those in the cliffs beside the Manning River at Kimbriki (Voisey, 1939a). These show the richly fossiliferous *Linoproductus springsurensis* and *Strophalosia jukesii* beds to advantage.

The greatest variety of rock types in this stage is to be found in the parish of Warbro between Willi Willi and Moparrabah, where tuffs, conglomerates, mudstones and a band of limestone occur (Voisey, 1934, 339).



Palæontology.

The fauna of the beds consists essentially of fenestellids, crinoids and brachiopods, notably *Linoproductus springsurensis* and *Strophalosia jukesii*. Numbers of *Spirifer*, *Martiniopsis*, *Dielasma*, *Productus* and *Platyschisma* are present as in most other Permian sections. *Ptychomphalina* and a number of species of *Aviculopecten* occur in the Tait's Creek Stage at Yessabah, while *Eurydesma cordatum*, *Aviculopecten mitchelli*, *Tæniothærus subquadratus* and *Cladochonus nicholsoni* are prominent in the Yessabah Stage. The identification of the trilobite *Phillipsia* is noteworthy as it is not included in Osborne's lists from the Hunter River Valley.

Although *Linoproductus springsurensis* is well spread through the sequence it forms two well-marked horizons, one below the Yessabah Limestone in the Fenestellidæ Mudstones and one in the Warbro Stage above the limestone. The absence of this brachiopod and *Cladochonus nicholsoni* from the Hunter Valley sequences and their abundance in the Manning-Macleay Province and in Queensland suggest that there was a land barrier south of the Manning River. This is also supported by the change in the character of the Yessabah Limestone around Kimbriki and the fact that the Gloucester Coal Measures rest directly upon the Carboniferous lavas in the Gloucester Trough (Voisey, 1940).

As full lists of fossils have been given in earlier papers (Voisey, 1936, 1939a), they will not be repeated here.

SUMMARY.

The Macleay Series in the Manning-Macleay Province, which corresponds with part at least of the Permian Lower Marine Series of the Hunter River Valley, has been divided into three stages on lithological grounds.

The sediments occur only in synclines and faulted blocks. Higher members of the sequence, if any were developed, are no longer preserved. The fossils *Linoproductus springsurensis* and *Cladochonus nicholsoni*, which have not been found in the Hunter Valley sections but are present in Queensland, together with changes in lithology, indicate a land barrier between the Manning and Hunter rivers in Permian times.

ACKNOWLEDGEMENTS.

I tender my grateful thanks to Dr. W. R. Browne for his help and inspiration freely given over many years.

My thanks are also due to the Commonwealth Government for financial help received from the Research Grant to the University of Sydney.

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PART II

37439

THE CHEMISTRY OF OSMIUM.

PART IV. THE PREPARATION AND RESOLUTION OF THE TRIS O,PHENANTHROLINE OSMIUM II ION.

By F. P. DWYER, D.Sc.,
N. A. GIBSON, M.Sc., A.R.I.C.,
and (MISS) E. C. GYARFAS, M.Sc.

Manuscript received, April 24, 1950. Read, June 7, 1950.

Tris 2 : 2' dipyridyl osmium II bromide was prepared by Burstall, Dwyer and Gyarfas (1950) by heating a mixture of ammonium bromosmate IV⁺ with 2 : 2' dipyridyl at 280° C. The dark green complex ion $\text{Os}(\text{dipy})^{++}$ was resolved through the antimonyl tartrate into stable optical enantiomorphs. The complex ion was reversibly oxidized at approximately 0.9 volt to the red $\text{Os}(\text{dipy})_3^{+++}$ ion, which was also obtained in stable optical forms (Dwyer and Gyarfas, 1950).

The corresponding osmium II compounds with o,phenanthroline were ultimately prepared by heating the base with ammonium bromosmate in glycerol solution at 280–300° C. Mixtures of potassium hexachlor or hexabromosmate IV or potassium hexachlorosmate III with phenanthroline in aqueous alcohol could not be reduced to the compound with hypophosphorous acid in the same manner as the ruthenium compound (Dwyer, Humpoletz and Nyholm, 1946). Heating of a mixture of excess base and ammonium bromosmate in the absence of solvents, either with or without reducing agents such as ammonium hypophosphite, sucrose, lactose or formaldehyde, gave only very poor yields of the substance associated with osmium metal, and a large amount of tarry carbonaceous matter.

The compound was isolated from the glycerol mixture, after dilution with water, by addition of potassium iodide, and the sparingly soluble iodide was crystallized several times to remove traces of a very dark brown impurity. The very sparingly soluble perchlorate was obtained from the iodide by treatment with sodium perchlorate, and the soluble chloride by treatment with silver chloride. The salts crystallized in dark brown needles or flakes with a green reflex. They dissolved in water to form intensely dark greenish brown solutions, which were stable to strong acids and alkalis. In nitric acid the solutions gradually became red as a result of oxidation to the ion $\text{Os}(\text{phenan})_3^{+++}$. The potential of the reversible reaction was approximately 0.9 volt. The oxidized solution, like the solutions of the ions $\text{Fe}(\text{phenan})_3^{+++}$ and $\text{Ru}(\text{phenan})_3^{+++}$, was not stable, and in the absence of excess oxidizing agent gradually became brown by the re-formation of the original osmium II complex ion.

The resolution of the tris o,phenanthroline osmium II ion was carried out in a similar manner to the ruthenium, iron and nickel complexes (Dwyer and Gyarfas, 1949), through the antimonyl tartrate. The dextro-form separated as the sparingly soluble antimonyl tartrate, which was transformed to the perchlorate. The lævo-perchlorate was obtained by addition of sodium perchlorate to the filtrate after the precipitation of the dextro-antimonyl tartrate. The complex ion was optically stable in boiling water, like the corresponding ruthenium compound. No rotation was observed in the NaD line, this wavelength being close to an absorption maximum.

The pure perchlorates gave $[\alpha]_{5461}^{25} = +3670^\circ$ and -3570° . The corresponding ruthenium and nickel complex perchlorates gave $[\alpha]_{5461}^{25} = \pm 1330^\circ$ and $\pm 1470^\circ$ respectively.

The optical forms were oxidizable with ceric sulphate to optically active forms of the osmium III complex $\text{Os}(\text{phenan})_3^{+++}$. It is hoped to be able to isolate the enantiomorphous forms of this complex ion in the solid form.

The redox potentials of this complex and the dipyridyl analogue will be discussed in a subsequent communication.

EXPERIMENTAL.

Tris o,Phenanthroline Osmium II Iodide Trihydrate.

Ammonium hexabromosmate (2.1 g., 1 mol.) in glycerol (40 ml.) was heated to $80-90^\circ\text{C}$. with stirring until the bromosmate had dissolved to a deep red solution. O,Phenanthroline monohydrate (3.6 g., 6 mols.) was added gradually at 120°C . and the mixture maintained at this temperature until the water was lost; then the temperature was raised to $250-270^\circ\text{C}$. whilst the mixture was stirred with a thermometer, and this temperature was maintained for 20 minutes. The dark brown mixture was cooled to below 100°C . and poured into 150 ml. of warm water. The mixture was acidified with hydrochloric acid (3-5 ml. of 5N.) and potassium iodide added. The dark greenish brown precipitate was washed with ether and ice water, and recrystallized several times from hot water and potassium iodide.

The substance crystallized in black flat flakes and prisms, was very soluble in methyl alcohol, but less soluble in ethyl alcohol and acetone.

Found: Os = 18.0%; I = 24.6%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{I}_3 \cdot 3\text{H}_2\text{O}$: Os = 18.3%; I = 24.4%.

Tris o,Phenanthroline Osmium II Chloride Octahydrate.

The iodide (1 g.) in hot water (50 ml.) was shaken for 15 minutes with excess of freshly precipitated silver chloride. After filtering from silver halide the dark greenish brown filtrate was evaporated to 5 ml. on the water-bath and then to dryness over calcium chloride in a desiccator. The substance crystallized in very dark brown prisms with a greenish reflex.

Found: Os = 20.1%; Cl = 7.47%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3\text{Cl}_3 \cdot 8\text{H}_2\text{O}$: Os = 20.1%; Cl = 7.50%.

Tris o,Phenanthroline Osmium II Perchlorate Dihydrate.

The iodide (*vide supra*) (1 g.) in hot water (100 mls.) was treated drop by drop with sodium perchlorate solution (10%) with scratching the sides of the vessel. The sparingly soluble perchlorate crystallized as a brown microcrystalline powder. It was very soluble in methylalcohol

Found: Os = 19.5%; N = 8.79%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: Os = 19.7%; N = 8.70%.

d,Tris o,Phenanthroline Osmium II d,Antimonyl Tartrate Trihydrate.

The iodide (1 g.) in hot water (50 ml.) was transformed to the chloride as above and the solution cooled. Potassium antimonyl tartrate (1 g., 3 mols.) in water (20 ml.) was added gradually with scratching of the sides of the vessel. The antimonyl tartrate of the dextro-form was precipitated in fine brown needles. These were removed by filtration, washed with ice water and then dissolved in cold 0.05N sodium hydroxide solution and after filtration reprecipitated with acetic acid and a few drops of saturated potassium antimonyl tartrate solution. This purification was repeated three times. The substance was sparingly soluble in water to a greenish brown solution, but easily soluble in dilute acids and alkalis.

A 0.006% solution in 0.01 NaOH gave $\alpha = +0.10^\circ$ (1 dm. tube), whence $[\alpha]_{5461}^{25} = +1700^\circ$.

Found: Os = 13.9%; N = 6.18%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{C}_6\text{H}_4\text{O}_6\text{SbO})_2 \cdot 3\text{H}_2\text{O}$: Os = 14.0%; N = 6.20%.

d, Tris o,Phenanthroline Osmium II Perchlorate Monohydrate.

The antimonyl tartrate above was dissolved in cold 0.05N sodium hydroxide and precipitated with sodium perchlorate solution (10%). The resulting precipitate was crystallized several times from hot water by the addition of sodium perchlorate. The substance crystallized in small dark brown rods with a green reflex. It was more soluble than the *d,l* perchlorate.

A 0.003% solution in water gave $\alpha = +0.11^\circ$ (1 dm. tube), whence $[\alpha]_{5461}^{25} = +3670^\circ$ and $[M]_{5461}^{25} = +34,800^\circ$.

In the sodium D line no rotation could be observed.

The solution was optically stable at room temperature and at 100° C.

Found : Os = 20.1% ; N = 8.93%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Os = 20.1% ; N = 8.87%.

l, Tris o,Phenanthroline Osmium II Perchlorate Monohydrate.

The filtrate from the precipitation of *d*, tris *o*,phenanthroline osmium II *d*,antimonyl tartrate (*vide supra*) was treated with sodium perchlorate solution and the resulting precipitate of the *lævo*-perchlorate crystallized several times from hot water with the addition of sodium perchlorate.

A 0.003% solution in water gave $\alpha = -0.10^\circ$ (1 dm. tube) whence $[\alpha]_{5461}^{25} = -3570^\circ$ and $[M]_{5461}^{25} = -33,800^\circ$.

Found : Os = 19.7% ; N = 8.95%.

Calculated for $\text{Os}(\text{C}_{12}\text{H}_8\text{N}_2)_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Os = 20.1% ; N = 8.87%.

SUMMARY.

Tris *o*,phenanthroline osmium II iodide was prepared by reaction between *o*,phenanthroline and ammonium bromosmate in glycerol solution at 250–270° C., followed by dilution with water and addition of potassium iodide. The intensely greenish brown solutions containing the ion $\text{Os}(\text{phenan})_3^{++}$ are reversibly oxidized to the red $\text{Os}(\text{phenan})_3^{+++}$ at approximately 0.9 volt. The enantiomorphous forms were isolated through the antimonyl tartrates, and the active perchlorates gave $[M]_{5461}^{25} = +34,800^\circ$ and $-33,800^\circ$.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss J. Fildes for nitrogen analyses and one of us (E.C.G.) to the Research Committee for an Assistantship.

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ON THE GRADING OF DUNE SANDS NEAR CASTLEREAGH, NEW SOUTH WALES.

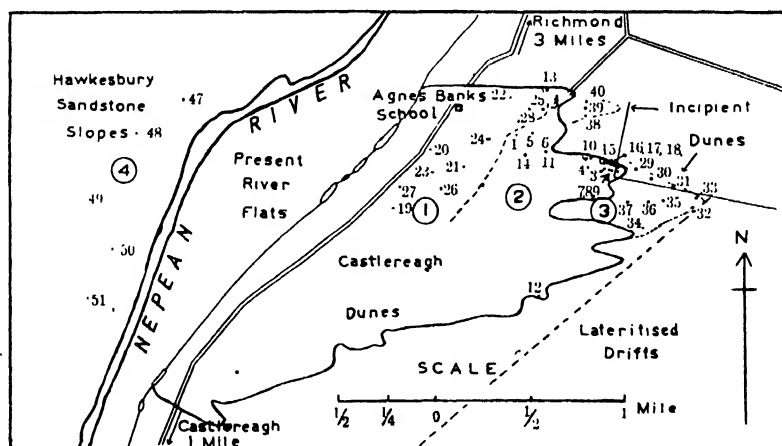
By D. S. SIMONETT, M.Sc.

With one map and three text-figures.

Manuscript received, April 12, 1950. Read, June 7, 1950.

In the western part of the Sydney Plain near the Nepean River at Castlereagh lies a small field of fixed longitudinal sand ridges. In an earlier paper (Simonett, 1949) it was concluded that these dunes were built up by westerly winds with sands derived from the Hawkesbury sandstone soils west of the Nepean; and that sand movement followed vegetation destruction on the sandstone, probably during the Early Recent arid period. It is now proposed to discuss the changes in grading wrought on the source soils during the dune building.

Crest and trough samples (33) were taken from the western and eastern parts of the dunes, respectively removed about $1\frac{1}{2}$ and $2\frac{1}{2}$ miles from the source. Five source soil samples were collected, together with 13 from the "Incipient Dunes", built up in advance of the main sand movement and composed of finer sands. The location of the samples is given in Map 1.

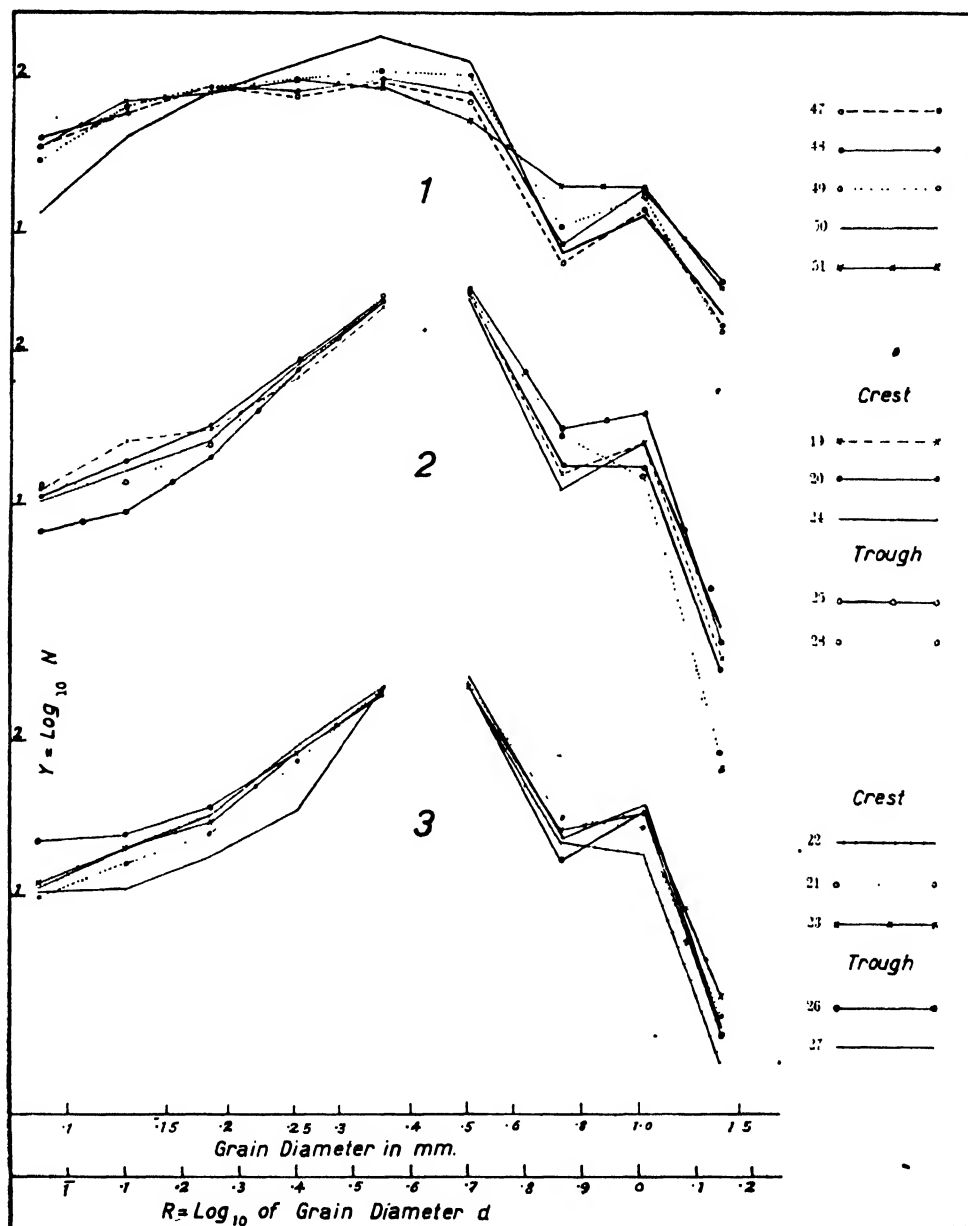


All the analyses obtained by dry sieving* were plotted graphically to enable ready comparisons of grain-size gradings; of these, 36 representative samples have been selected and plotted on a series of seven graphs.

* 100 gm. samples were taken, organic matter destroyed by boiling with hydrogen peroxide, and after thorough dispersion and decantation of particles smaller than 0.02 mm. the sands were oven-dried and sieved in a nest of Tyler sieves for 15 minutes on a Tyler "Ro-Tap" sieving machine. The following meshes were used (apertures in millimetres):

14 (1.168); 20 (0.888); 28 (0.589); 35 (0.417); 48 (0.295); 65 (0.208); 100 (0.147); 150 (0.104); 200 (0.074).

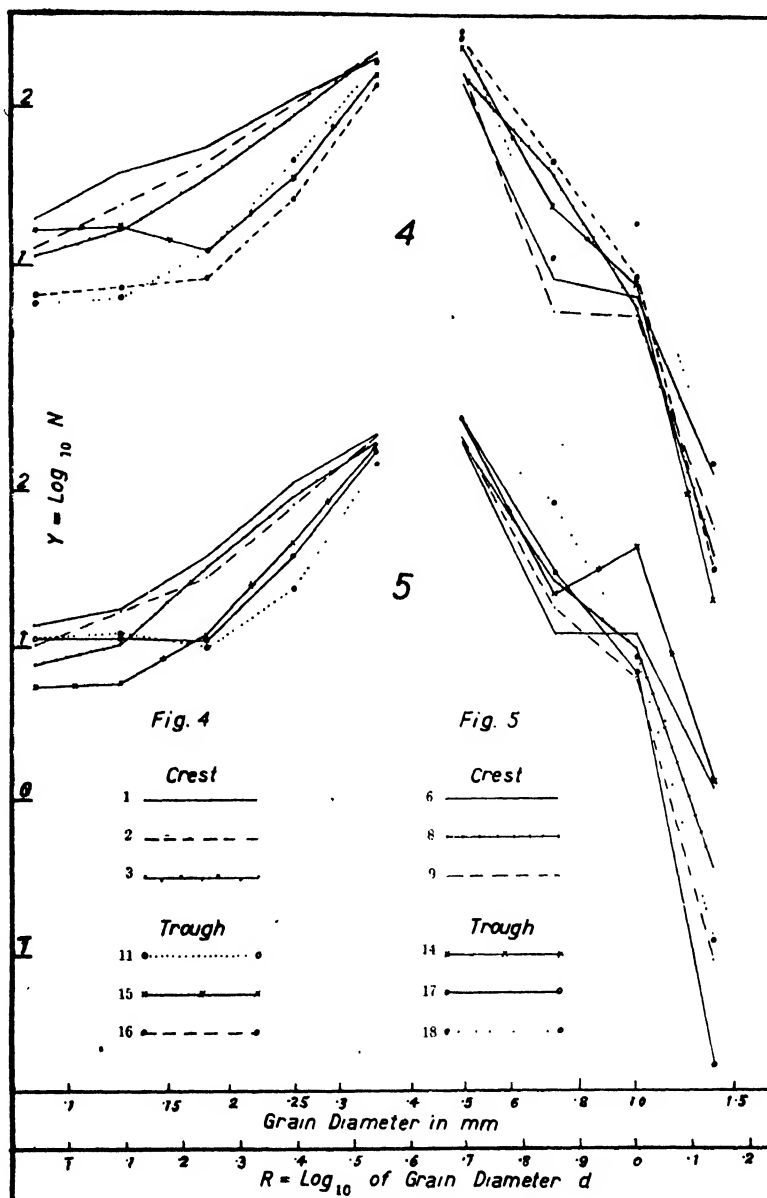
Bagnold's (1941) method of plotting these results was selected† for, using it he found that in naturally wind-blown sands "outside a definite central zone the grades to right and left of the peak (diameter) fall off each at its own constant rate". To those wind-blown sands whose grading conformed to this simple



arrangement of two straight lines inclined upwards, meeting at an apex, the top of which was replaced by a small arc, he applied the term *regular sands* whether the arrangement was symmetrical about the peak or not (*loc. cit.*, p. 118).

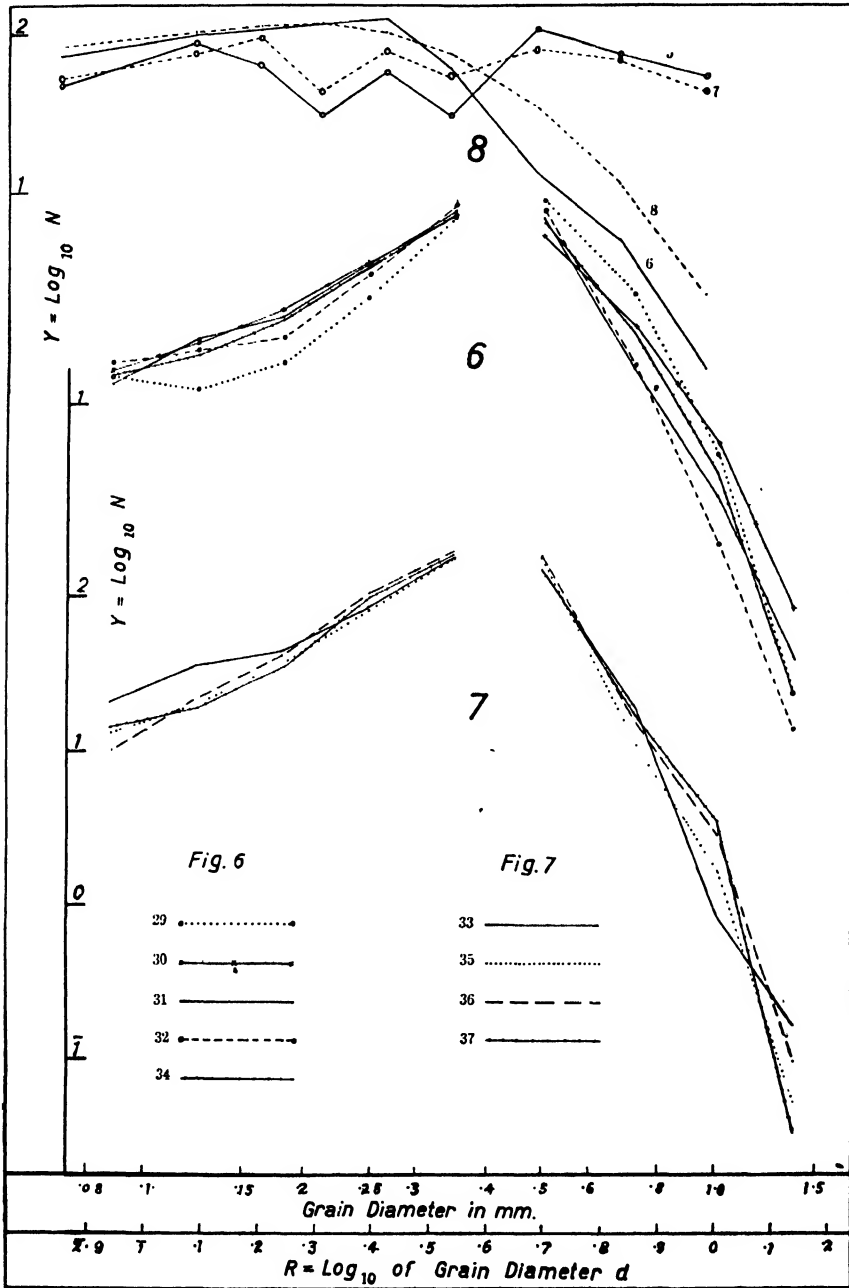
† The logarithm of the percentage-weight of sand per unit of the log. diameter scale is plotted as ordinate against an abscissa of the log. grain diameter.

Considering the grading of each group. The five source samples plotted in Figure 1 show the same characteristic grading, the most distinctive features of which are the marked irregularity on the coarse side and the gentle fall away from the peak on the fine side with a slight steepening to the finest grades.



The western group of sands, Figures 2 and 3, moved a mile to $1\frac{1}{2}$ miles, have altered in grading to approach regularity, particularly about the peak diameter, but on the coarse side the initial excess of sands of the range 0.888–1.16 mm. over that of 0.589–0.888 has been but tardily removed (only samples 22, 24 (crest) and 28 (trough) show any significant reduction) and these are the easternmost samples of this group. The steepening in the finest grades of the parent

sand has, however, not only been removed, but has been replaced by a slight flattening in the trough samples. Other than this little difference in crest and trough grading is evident at this stage.



In the eastern sands (a further half to one mile removed from the source), Figures 4 and 5, the changes which were barely evident in the western analyses are pronounced, and a considerable difference in trough and crest grading is to

be seen, the finer sands collecting on the ridges and coarse sands in the troughs. From all the crests the excess of the penultimate grade over that retained on sieve 28 has been eliminated ; but the curve is still kinked at this point. On the other hand in only those trough samples farthest from the source has this occurred.*

The crest sands are near-regular on both fine and coarse sides of the grading but the trough samples are not, for the slight flattening in the finest grades in the trough samples of the western sands is now very marked in the eastern trough sands.

The "Incipient Dunes" sands are essentially regular and lack both the coarse side distortion and the fine side flattening of the true sand dunes (Figures 6 and 7).

DISCUSSION.

It seems evident from the analyses that although the rate of removal of the initial distortion in the coarse grading of the source soils differed slightly in the crest and trough samples (the former approaching regularity a little earlier than the troughs) both required between two and three miles transport for such removal.

These results are interesting when compared with work along similar lines by Bagnold (1941) and Chepil (1946).

Bagnold (1941, 142-3), working with a regular sand distorted in the ultimate fine and coarse grades by the addition of excess sand, found in the wind tunnel that the excess in the finest grades was "hardly (removed) at all in the accretion deposits" by wind action, whilst that on the coarse-side was rapidly removed. On the basis of this experiment he concluded that "the processes . . . which tend to produce the logarithmic relation between the proportion by weight and the grain diameter, are different on the fine and coarse sides of the grading, though both must occur in the early part of the cycle of movement".

Chepil (1946), working in the Canadian Wheat Belt, analysed sands piled into small dunes resulting from drift from eroding cultivated fields of a quarter to half a mile in length. He found that "except for a few slight kinks, the two arms of each curve are straight lines and agree, at least in essential features, with the grading diagrams found by Bagnold for desert sand. Such marked and consistent grading of drift material seems almost incredible in view of the fact that the materials deposited in dunes were in the majority of cases the result of a single dust storm" and concluded that "a distance (of a quarter to half a mile) was apparently sufficient for effecting an ultimate selection of the blown materials".

A greater distance was needed to remove the coarse-side distortion at Castlereagh than would have been expected on the basis of Bagnold's and Chepil's results. Comparing the diameter of the Castlereagh distortion (1.0 mm.) with the latter (0.5-0.65 mm.) an even earlier removal than Chepil's might have been expected. Clearly some factor must have retarded the sorting. In part the discrepancy with Bagnold's experiment (*loc. cit.*, pp. 142-3) may be explained by his use of a regular source sample distorted only in the ultimate grades ; *i.e.* one which would reach regularity very quickly. However, this argument cannot apply to Chepil's irregular source samples (Figure 8). It is more likely that the answer lies in the amount of sand in movement, the speed of sorting depending on the continuity of supply of irregular sand from up-wind. With

* With the exception of the most easterly trough samples from which the irregularity has been shifted (16, 17, 18) all the trough samples retain the irregularity to a greater degree than crest samples moved an identical distance. The following pairs of trough and crest samples have been moved the same distance : all are less regular in the troughs than the crests :

4C : 10T ; 1 : 5 : 14 ; 6 : 11 ; 3 : 15 ; 2 : 13.

large volumes of sand available for movement fresh sand containing the coarse-side irregularity would continually be moving over the areas in which this coarse-side excess remained as residuals from earlier movement emphasizing the irregularity and in effect shifting the removal-bed down wind. All the evidence at Castlereagh points to large volumes of sand available (Simonett, 1949), a situation far less likely in the heavier wheat soils studied by Chepil. The similarity of grading of "Incipient Dune" sample 39 moved half a mile less than the other samples of Figure 6 (see also Map 1) supports this view. It is possible that with certain initial gradings and large masses of sand for transport the attainment of regularity may be even longer delayed than at Castlereagh.

The significance of the marked flattening in grading in the finest sands of the eastern trough samples is not easily determined. We cannot regard it as an unremoved initial irregularity, for the reverse was the case in the parent sand where the grading steepened slightly to the finest grades. It is clearly a feature produced on movement and appears to be fundamental to at least the early process of grading of the trough samples.

The suggestion is made that this flattening, which it will be seen occurs in sieves 150 (0.104–0.147 mm.) and 200 (0.074–0.104 mm.), may be due to the fact that about this diameter (0.08 mm., Bagnold, *loc. cit.*, p. 88) the fluid threshold for grain movement is closest to the impact threshold, and thus particles of diameter 0.10–0.15 mm. (Chepil, 1945, p. 404) are the most readily eroded and maintained in saltation of all grades. Thus with greater wind sorting at the crests any excess of the fine grades would tend to be directed outwards to the troughs, where decline in wind velocity would favour deposition.

The concentration of fine grades of this diameter in the troughs is interesting when compared with the peak diameters of the crest and trough sands of the Simpson Desert seif dunes analysed by Carroll (1944) and Crocker (1946). They found that the coarsest sands collected on the crests (peak 0.17 mm., one 0.35 mm.) and the finest in the troughs (peak 0.85–0.9 mm.). On the other hand at Castlereagh the eastern crest sands (peak load-sieve 48/0.295 mm. 31–36%) are finer than the trough sands (peak load sieve 35/0.417 mm. 45–53%). Bagnold (*op. cit.*, p. 228) found the fine-crest-coarse-trough relationship to be characteristic of the Libyan seif dunes and postulated it as general. Crocker (1946) suggested that the reversal of the relationship in the Simpson Desert sands may be due to their extreme fineness and their concentration about the critical diameter of 0.08 mm. They are undoubtedly much finer than the Castlereagh sands or all the examples Bagnold gives of typical Libyan Desert gradings.

On the evidence available at Castlereagh we cannot say that the extreme fine-side distortion of the eastern trough sands is more than a feature of the early part of the process of grading. However, the fact that the fine-side distortion in the Castlereagh trough samples occurs in the same diameter range as the peak diameter of the Simpson Desert trough samples suggests that it is more than an early phase in the grading cycle and may be in fact fundamental to the whole process. The reason for the concentration of these grades (0.08–0.15 mm.) in the troughs appears to be bound up with the ease with which they are moved; gentle winds in particular capable only of moving sand on the crests would ensure their selective migration to the troughs.

Madigan (1946, p. 62) suggested that the concentration of these grades in the troughs in the Simpson Desert was a post dune-fixation phenomenon—"the higher percentage of fine grades and clay particles in the two inter-ridge samples as compared with crests is probably due to the winnowing effect on the crests, where under present conditions of no set lateral movement and secondary winds from both sides the coarser fractions will tend to remain as residuals on the crests and the crest sand to become more regular than that in the lanes. The

"smoking" effect in strong lateral winds will carry the dust and fine particles well down into the lee of the ridge, where it will remain". This process can equally well take place during the dune-building and may be regarded as a normal dune process.

With wide source sample gradings double maxima (one fine 0.08 mm., and one coarse) should occur in the gradings of the lower slopes of seif dune plinths in young deserts where the dunes are closely spaced. Thus in the grading of sands from the Kalahari longitudinal dunes analysed by Lewis (1936) (Table 1) the concentration of sands finer than 0.15 mm. in the lower slopes and troughs is marked. The tendency to another peak in these gradings coarser than the peak of the crest gradings is also evident.* On the other hand with narrow source sands one or other of the maxima would be damped. The Simpson Desert sands are low in coarse grains and lack a definite coarse maximum in the troughs.

Geological time must be considered as a factor affecting gradings. In young dune fields (Kalahari) with low, closely spaced dunes, fine grades will mantle the lower dune slopes as well as the troughs; but in old seif dune fields long continued winnowing of steep-sided massive dunes, miles apart as in Libya, would move all the fine grades into the sand sheet between the dunes. An uncomplicated fine-crest-coarse-lower-slope grading relationship as described by Bagnold would result on the dunes, the intervening sand plain consisting of the very fine grades and residual very coarse grades.

No one simple general rule can characterize either rate of removal of irregularities or the grading relationships on dunes. It may be misleading to apply results obtained from wind-tunnel and field tests on removal of irregularities, where sands were driven away from a source area, to desert areas such as the Simpson where Madigan has shown that many of the dunes arose *ab initio* from a sand sea. Equally, grading relationships on seif dunes will be a function of origin (*ab initio* dunes or dunes trailing from a windward source) grading of the source sands, and maturity of the dune system. The attempt above to indicate the general types of gradings that are likely to occur in a limited group of circumstances must be considered speculative; a generalized theory of dune grading must, however, take all the factors considered above into account.

SUMMARY

The rate of removal of irregularities on the coarse side of the grading appears to vary with the amount of sand in movement. Concentration of grades of the diameter range 0.08–0.15 mm. in the troughs of the Castlereagh longitudinal dunes and also in the troughs of desert young seif dune fields (Kalahari, and Simpson deserts) appears to be a normal feature of the grading of closely spaced seif dune fields. Grading relationships on longitudinal dunes will be a function of the maturity of the system, the width of the grading of the source sands, and the origin of the dunes (*ab initio* dunes arising in a sand sea, or dunes trailing from a limited windward source).

ACKNOWLEDGEMENTS.

Grateful acknowledgement is made to Mr. H. J. Vogan, of the Civil Engineering Department, University of Sydney, for the use of the Tyler "Ro-Tap" sieving machine.

* The results given in Table 1 (appendix No. 1 of Lewis's paper) are mean analyses. About 200 samples were analysed from ten localities for crests, slopes and corridors of the dunes. Thus 30 groups of means are available, about six samples to a mean, assuming uniform sampling from all localities. This lumping of analyses together must make one suspicious of the value of Lewis's results. However, since all ten groups possess roughly similar gradings, a certain amount of value may be given to them, though they must be used with caution.

TABLE 1.
(After Lewis, 1936.)
Mechanical Analyses of Sands.
Kalahari Sand Dunes.
Mean of all Readings.

Percentages by weight retained on each sieve.

| 14 | 28 | 40 | Number of Sieve. | | | 90 | 115 | 150 | Passing 150 | Remarks. |
|--------------------|----|----|------------------|----|----|----|-----|-----|----------------|----------|
| 1. Houmoed. | | | | | | | | | | |
| — | — | 5 | 15 | 29 | 19 | 14 | 9 | 9 | Slopes. | |
| — | — | 2 | 21 | 44 | 20 | 9 | 3 | 1 | Crests. | |
| 2 | 5 | 10 | 9 | 16 | 15 | 13 | 12 | 18 | Straats. | |
| 2. Lentlands Pan. | | | | | | | | | | |
| — | — | 1 | 8 | 29 | 24 | 22 | 9 | 7 | Slopes. | |
| — | — | — | 10 | 42 | 28 | 14 | 4 | 2 | Crest. | |
| — | — | 6 | 19 | 27 | 18 | 15 | 7 | 8 | Staat. | |
| 3. Kakolk. | | | | | | | | | | |
| — | — | 5 | 7 | 20 | 22 | 18 | 16 | 12 | Slopes. | |
| — | — | 4 | 22 | 31 | 21 | 12 | 7 | 3 | Crest. | |
| — | 8 | 16 | 6 | 10 | 12 | 13 | 14 | 21 | Staat. | |
| 4. Abiquas Puts. | | | | | | | | | | |
| — | — | 1 | 3 | 21 | 17 | 28 | 13 | 17 | Slopes. | |
| — | — | — | 4 | 25 | 25 | 24 | 13 | 9 | Crest. | |
| — | — | 2 | 3 | 12 | 11 | 17 | 18 | 37 | Staat. | |
| 5. Albion. | | | | | | | | | | |
| — | 2 | 12 | 9 | 16 | 18 | 18 | 12 | 13 | Slopes. | |
| — | — | 6 | 13 | 27 | 23 | 18 | 9 | 4 | Crest. | |
| 3 | 2 | 9 | 9 | 17 | 18 | 17 | 11 | 14 | Staat. | |
| 6. Gemsbok Plains. | | | | | | | | | | |
| — | — | 2 | 17 | 38 | 19 | 14 | 6 | 4 | Slopes. | |
| — | — | 1 | 14 | 41 | 22 | 13 | 6 | 3 | Crest. | |
| — | 2 | 9 | 21 | 25 | 13 | 12 | 8 | 11 | Staat. | |
| 7. Bushmans Puts. | | | | | | | | | | |
| — | 1 | 6 | 10 | 20 | 17 | 19 | 13 | 14 | Slopes. | |
| — | — | 2 | 8 | 25 | 22 | 21 | 12 | 10 | Crest. | |
| — | 3 | 10 | 11 | 17 | 14 | 17 | 12 | 16 | Staat. | |
| 8. Tellery Pan. | | | | | | | | | | |
| — | — | 1 | 7 | 21 | 22 | 22 | 16 | 11 | Slopes. | |
| — | — | 2 | 13 | 32 | 22 | 17 | 10 | 4 | Crest. | |
| — | 1 | 6 | 10 | 18 | 16 | 16 | 17 | 16 | Staat. | |
| 9. De Hoek. | | | | | | | | | | |
| — | — | 3 | 6 | 22 | 21 | 23 | 12 | 13 | Slopes. | |
| — | — | — | 6 | 40 | 24 | 21 | 6 | 3 | Crest. | |
| — | 2 | 7 | 6 | 14 | 15 | 20 | 16 | 20 | Staat. | |
| 10. Debinga. | | | | | | | | | | |
| — | 5 | 15 | 9 | 10 | 11 | 19 | 16 | 15 | Slopes. | |
| — | 2 | 10 | 11 | 13 | 13 | 23 | 17 | 11 | Crest. | |
| 2 | 12 | 16 | 6 | 7 | 8 | 18 | 15 | 16 | Staat. | |

Sieve apertures in mms. are as below :

14 (1·168), 28 (0·589), 40 (0·381), 48 (0·295), 65 (0·208), 90 (0·150), 115 (0·124), 150 (0·102).

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THE CHEMISTRY OF OSMIUM.

PART V. THE REDOX POTENTIALS OF THE TRIS 2 : 2'-DIPYRIDYL OSMIUM II/III AND THE TRIS O,PHENANTHROLINE OSMIUM II/III COUPLES.

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Manuscript received, May 10, 1950. Read, July 5, 1950.

Tris 2 : 2' dipyridyl osmium II salts and analogous o-phenanthroline compounds (Burstall, Dwyer and Gyarfas, 1950 ; Dwyer, Gibson and Gyarfas, 1950) are reversibly oxidized to the corresponding osmium III complexes. The potentials of the two reactions have now been determined in order to complete the iron, ruthenium and osmium triad of such complexes, as well as to ascertain the suitability of the compounds as redox indicators.

The oxidized form of the dipyridyl compound was sufficiently stable to be obtained in solution in known concentration, hence the potential could be obtained by the standard method of allowing an electrode to come to equilibrium in an equimolar mixture of oxidant and reductant. The oxidized form of the phenanthroline complex, however, was unstable and rapidly underwent reduction. This reaction has already been noted with the oxidized forms of the iron and ruthenium complexes with o-phenanthroline (Dwyer and McKenzie, 1947 ; Dwyer, Humpoletz and Nyholm, 1946). The potential of the phenanthroline complex was determined by exactly half oxidizing a standardized solution of the reduced form and observing the maximum potential attained on an electrode (Dwyer, 1949).

Both systems were typically cationic, the potentials decreasing with increasing ionic strength. At the same ionic strengths, the potentials of the phenanthroline complex were slightly higher. This follows the same trend as with the iron and ruthenium compounds. However, unlike the Fe and Ru compounds, the stability of the oxidized form decreased with increasing acid concentration.

With the completion of the potential investigations of the 2 : 2' dipyridyl and o-phenanthroline complexes with the members of the iron triad, it is interesting to compare the potential changes consequent upon complex formation. The figures shown in detail in Table I are approximate, since corresponding potentials of the simple bivalent/trivalent system and the bivalent:trivalent complex system are not available in some instances at the same ionic strength. The maximum potential change occurs with the ruthenium compounds, from +0.085 volt for the $\text{Ru}^{++}/\text{Ru}^{+++}$ couple to 1.31 volt for the $\text{Ru}(\text{phenan})_3^{++}/\text{Ru}(\text{phenan})_3^{+++}$ system, a change of 1.225 volts. The potential change consequent upon the formation of the osmium compounds cannot be stated with any degree of accuracy. The potential of the system $\text{Os}^{++}/\text{Os}^{+++}$ is unknown, and probably cannot be determined directly, since disproportionation of the Os^{++} ion can be expected to occur. With an estimated value of -0.25 volt, the change is of the order of 1.13 volts for the formation of the phenanthroline complex.

TABLE I.

| | Potential M^{++}/M^{+++} . | Potential Dipyridyl Complex. | Potential Change. | Potential Phenan. Complex. | Potential Change. |
|----------|---------------------------------|------------------------------------|----------------------|----------------------------------|----------------------|
| Fe | +0.75 V. ¹ | +1.096 V. ² | 0.346 V. | +1.120 V. ² | 0.370 V. |
| Ru | +0.085 ³ | +1.30 ⁴ | 1.315 | +1.31 ⁴ | 1.325 |
| Os | -0.25 ⁵ | +0.878 | 1.128 | +0.877 | 1.127 |

¹ Thermodynamic value, 0.771 V. (Latimer, 1940.)² Dwyer and McKenzie, 1947.³ Backhouse and Dwyer, 1949.⁴ Dwyer, 1949.⁵ Estimated value.

Two general observations are noteworthy: the stability of the reduced form is the greater with phenanthroline; and of the oxidized form with dipyridyl. The iron compounds in both oxidized and reduced states are less stable chemically and optically than the ruthenium and osmium compounds.

EXPERIMENTAL.

The redox potential determinations were carried out at 25° C. in the apparatus used for previous determinations (Dwyer, McKenzie and Nyholm, 1940). The saturated calomel electrode was calibrated against quinhydrone in potassium hydrogen phthalate solution, pH 4.00, using a gold electrode. The value of the potential accepted for the latter electrode was 0.4623 V. at 25° C. The equimolar solutions of tris 2:2' dipyridyl osmium II and osmium III perchlorates were prepared by making 0.001 M solution of the reductant, dividing into two portions, and oxidizing one portion with a slight excess of chlorine. The excess chlorine was then expelled by a rapid current of air saturated with water. The absence of chlorine was shown by taking 10 ml. of the pink oxidized solution and adding one drop of the deep green reduced solution. The consequent colour change showed that chlorine was absent. Equal volumes of the oxidized and reduced solutions were then mixed. Water and acid were subsequently added, so that the final solution was M/4000 with respect to oxidant and reductant ion.

The tris o-phenanthroline osmium II perchlorate was prepared in saturated aqueous solution, approximately M/1300, diluted with water and acid to twice the volume, and potentiometrically titrated with 0.01 N potassium permanganate, or in the first determination (with no added acid), with dilute chlorine water. The volume of permanganate needed to half oxidize the solution was thus obtained. Immediately following, another solution was prepared with added acid and water and the calculated volume of permanganate so that the concentration of oxidant and reductant was M/5200 each. A platinum electrode in the mixture was read each minute until the maximum value was obtained. For acid concentrations of 0.05 N and 0.1 N the maximum was stable for more than one and a half hours. With stronger acid the time of duration of the maximum decreased, so that with 1 N acid the potential commenced to fall in the first minute.

With the osmium dipyridyl system, the potential was stable for some hours up to an acid concentration of 1 N, when a decrease of 35 mV. occurred in fifteen hours. With the stronger acid concentrations 2 N, 3 N and 5 N, the potentials decreased after a few minutes. The potentials observed are shown in Table II.

TABLE II.

| Acid Conc. (Normality). | Os(dipy) ₃ ⁺⁺ /Os(dipy) ₃ ⁺⁺⁺ | Os(phenan) ₃ ⁺⁺ / Os(phenan) ₃ ⁺⁺⁺ |
|----------------------------|---|---|
| None added | 0.877, V. | 0.877 V. |
| 0.05 | 0.863 ₁ | 0.863 ₇ |
| 0.1 | 0.855 ₇ | 0.859 ₃ |
| 0.2 | 0.847 ₃ | 0.856 ₄ |
| 0.5 | 0.833 ₁ | 0.842 ₁ |
| 1.0 | 0.819 ₇ | 0.822 ₆ |
| 2.0 | 0.802 | — |
| 3.0 | 0.775 | — |
| 5.0 | 0.727 | — |

SUMMARY.

The redox potentials of the two systems tris 2:2' dipyridyl osmium II/tris 2:2' dipyridyl osmium III, and tris o-phenanthroline osmium II/tris o-phenanthroline osmium III have been determined. Both systems were found to be typically cationic. The potentials respectively in 0.1 N hydrochloric acid were 0.8557 and 0.8593 volt.

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THE CHEMISTRY OF OSMIUM.

PART VI. THE USE OF TRIS O-PHENANTHROLINE OSMIUM II PERCHLORATE AS AN INTERNAL REDOX INDICATOR.

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Manuscript received, May 10, 1950. Read, July 5, 1950.

The first internal redox indicator for the titration of ferrous iron with potassium dichromate was diphenylamine (Knop, 1924). Analogous compounds—diphenylamine sulphonic acid and diphenyl benzidine—have been recommended in order to overcome the relatively diffuse end-point and poor stability of prepared solutions of the diphenylamine reagent. The redox potential of all of these indicators is approximately 0.8 volt—hence the normal ferrous/ferric potential (0.7 volt) must be lowered by the addition of phosphoric acid or sodium fluoride in order to prevent the overlapping of the potentials of the indicator and the iron system. Tris 2:2' dipyridyl ferrous sulphate and later tris o-phenanthroline ferrous sulphate were recommended by Walden, Hammett and Chapman (1931) as more suitable reagents. In strongly acid solution (approximately 4 normal) the redox potentials of these indicators are 0.92 and 1.03 volt, and the titration of both the ferrous iron and the indicator can be carried to completion. The reduced form of the indicator, however, is unstable in acid of such high concentration, and the disappearance of the red colour of the indicator, which signals the end of the titration, can well be due to decomposition. In solutions of lower acid concentration, the maximum potential available from the dichromate is insufficient to effect the complete oxidation of the indicator, the potential of which is higher in weakly acid solution (1.102 volts in 0.1 N acid; Dwyer and McKenzie, 1947). A number of substituted dipyridyl complexes with ferrous iron were recently prepared by Smith (1949), who suggested that the ideal redox indicator for the ferrous/dichromate titration should have a potential of 0.85 volt.

Tris 2:2' dipyridyl osmium II perchlorate and the corresponding o-phenanthroline compound have been shown recently to be reversibly oxidized at a potential of 0.86 volt in 0.1 N acid (Dwyer, Gibson and Gyarfas, 1950). The colour changes accompanying oxidation were intense green to pink and intense brown to pink respectively. The conditions for the use of these substances as indicators for the ferrous/dichromate titration were determined by the standard procedure of carrying out mixed potentiometric titrations of ferrous sulphate and each of the osmium complexes as the perchlorate in sulphuric acid of varying concentrations.

The titration in 0.1 N acid gave a satisfactory end point "break" for the iron titration system, but not for either of the indicators (Fig. 1a). Both the ferrous/ferric and the osmium II complex/osmium III complex systems are cationic and the potentials fall with increasing ionic strength—but the decrease is greater with the osmium complex system and as a result both systems tend to merge. By the addition of either phosphoric acid or sodium fluoride in 1 N acid, both of these systems were satisfactorily separated.

It is to be noted that since the reduced form of the indicator is very much darker than the oxidized form, the visual end point does not coincide with the potentiometric end-point, but is about 30 to 50 mV. higher.

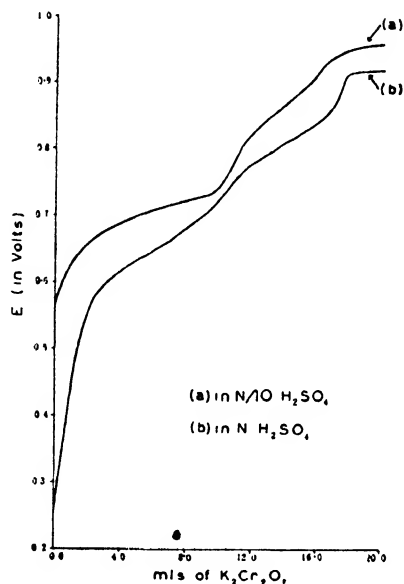


Fig. 1.

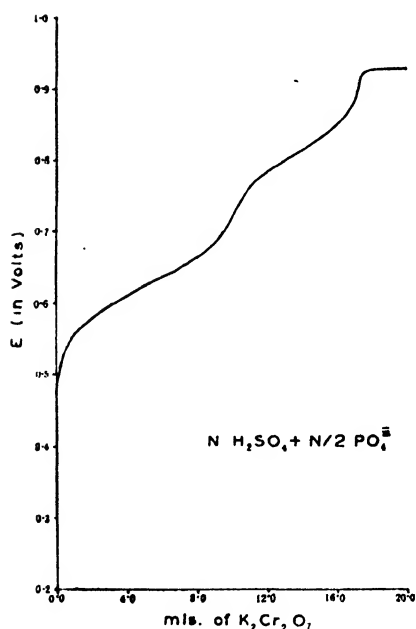


Fig. 2.

Under the latter conditions both osmium complexes were shown to be satisfactory indicators from the point of view of the potential. However, the

colour change of the tris 2 : 2' dipyridyl compound in the presence of chromium sulphate from deep green to a paler green was difficult to detect. The colour change of the o-phenanthroline complex from yellow-green to blue-green was well marked and easily detected.

In titrations involving 0.01 N potassium dichromate, the end point was diffuse, but excellent with the 0.1 N reagent. From a series of titrations it was found that with tris o-phenanthroline osmium II perchlorate the mean error was 0.1%.

EXPERIMENTAL.

The Potentiometric Titration of Ferrous Sulphate and the Complex Osmium II Perchlorates.

The titrations were carried out at 25° C., with a bright platinum electrode in the redox assembly used in previous work (Dwyer, McKenzie and Nyholm, 1944). The ferrous sulphate solution (10 ml., 0.01 N) was mixed with the indicator solution (100 ml., 0.01 M $\text{Os}(\text{dipy})_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, or 0.0078 M $\text{Os}(\text{phenan})_3(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$), and the required volume of sulphuric acid (10 N). The potassium dichromate (0.01 N) also contained the same concentration of sulphuric acid. Typical curves are shown in Figs. 1a, 1b and 2.

The Estimation of Ferrous Iron with Tris o,Phenanthroline Osmium II Perchlorate as Indicator.

Various volumes of standard ferrous sulphate solution were diluted with sulphuric acid so as to produce approximately 100 ml. of normal acid solution. Syrupy phosphoric acid (3 ml.) was added, and saturated (0.0078 M) tris o-phenanthroline osmium II perchlorate (2 ml.). The mixture was titrated with standard 0.1 N potassium dichromate solution. For comparison, the titration was carried out also with diphenylamine solution (1%) as internal indicator, using the recommended procedure (Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, Green & Co., London, 1947). The results are summarized in Table 1.

TABLE I.

| Mass Fe Taken. | Fe Found ($\text{Os}(\text{phenan})_3(\text{ClO}_4)_2$). | Percentage Error. | Fe Found (Diphenylamine). | Percentage Error. |
|----------------|---|-------------------|------------------------------|-------------------|
| 0.0692 g. | 0.0690 g. | -0.3 | 0.0701 g. | +1.3 |
| 0.1039 g. | 0.1039 g. | 0.0 | 0.1047 g. | +0.8 |
| 0.1385 g. | 0.1388 g. | +0.2 | 0.1393 g. | +0.6 |
| 0.1731 g. | 0.1731 g. | 0.0 | 0.1739 g. | +0.5 |
| 0.2077 g. | 0.2077 g. | 0.0 | 0.2088 g. | +0.5 |
| 0.2770 g. | 0.2770 g. | 0.0 | | |
| 0.3462 g. | 0.3459 g. | -0.1 | | |
| | | Mean | | Mean |
| | | 0.1% | | +0.7% |

SUMMARY.

Tris o-phenanthroline osmium II perchlorate is recommended as an internal redox indicator for the determination of ferrous iron with potassium dichromate. The reagent, used in the form of its saturated aqueous solution, is stable. The titration is performed in normal acid solution in the presence of phosphoric acid. An accuracy of $\pm 0.1\%$ is obtained.

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THE ESSENTIAL OIL OF *BÆCKEA CRENULATA* (DE CANDOLLE).

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The botany of this Myrtaceous shrub is described in Bentham's "Flora Australiensis", Vol. 3, pages 71-78. It is a small heath-like shrub with nearly round leaves about $\frac{1}{4}$ in. long, the edges of which are minutely crenulate. They grow in irregular fashion around the stem, and give to the plant a distinctive appearance. The plant, which has small white to pink flowers, occurs in patches along the coast of New South Wales into Queensland, and on the Blue Mountains of New South Wales. At one time it was very plentiful on most of the headlands of our popular seaside resorts, extending from Broken Bay in the north to Ulladulla in the south. Some of the localities between the north head of Port Jackson and Cronulla, where collections were made during the past quarter of a century, have since been cleared for building purposes. A pleasant odour of terpenes, modified by linalool, is readily detected on crushing the leaves between the fingers.

ESSENTIAL OIL.

Although the essential oil was examined first in 1921, its investigation has been continued to the present time. Little difficulty was experienced in isolating and identifying the principal terpenes, but the authors suspected others which have defied identification. Repeated efforts, using fresh samples of oil distilled from material collected from widely different localities during the past 27 years, have merely confirmed the original results. Quite recently, fresh samples of oil were distilled, but notwithstanding the use of improved methods of fractional distillation, no additional terpene constituents could be identified. It was possible, however, by the use of the Lecky-Ewell and Bower-Cooke fractionating columns, to isolate and identify the alcohol linalool, whose presence, although previously suspected, had not been established beyond doubt.

The essential oils from all consignments, obtained in yields of 0.2% to 0.36%, varied in colour from a lemon tint to deep brownish yellow, and possessed a pleasant, characteristic odour of the principal terpene constituents, modified by that of the alcohol, linalool. The corks of the containing vessels were readily bleached. On standing, many of the oils deposited yellow prismatic crystals of the phenol ether bæckeol, $C_{13}H_{18}O_4$, m.p. 103-104°.

Although bæckeol has been found in other Australian essential oils (Penfold, 1925) it was first isolated from the essential oil of *B. crenulata* in 1922 (Penfold and Morrison, 1922). The chemical deportment and constitution of this unique substance were described in a further communication to the Society in 1937 (Penfold and Morrison, 1937). Bæckeol was synthesised simultaneously by two groups of workers in 1940 (Ramage and Stowe, 1940; Hems and Tod, 1940).

The principal constituents, which have so far been identified, are as follows, viz.: *d*- α -pinene, *d*- and *dl*-limonene, γ -terpinene, cymene, linalool, sesquiterpenes and bæckeol.

Baekea crenulata (De Candolle).

| Date. | Localities (in New South Wales). | Weight of Leaves. Lb. | Yield of Oil. % | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ | Solubility in 80% Alcohol. (W/W.) | Ester Number after 1½ hours Hot Sap. | Ester Number after Acetyla- tion. | Remarks. |
|--------------------|--|-----------------------------|-----------------------|-----------------------|-------------------------|--------------------|--|--|---|---|
| 1921 20/ 3/1922 | Waverley .. Long Bay .. | 7 108½ | 0.2 0.2 | 0.8606 0.8923 | +15° +28.65° | 1.4777 1.4800 | 10 Vol. 8 Vol. | | | |
| 7/ 2/1933 | Ulladulla .. | 150 | 0.32 | 0.8704 | +25.8° | 1.4776 | 7 Vol. | 12.7 | 47.6 | |
| 8/ 8/1934 | Ulladulla .. | 212 | 0.2 | 0.8778 | +21.85° | 1.4813 | 10 Vol. | 11.5 | 46.7 | |
| 3/ 2/1936 | Malabar .. | 196 | 0.28 | 0.8995 | +24.8° | 1.4830 | 8 Vol. | 28.6 | 87.2 | |
| 9/ 8/1938 | Ulladulla .. | 226 | 0.28 | 0.8735 | +27.63° | 1.4773 | 9 Vol. | 11.0 | 43.6 | |
| 23/ 9/1940 | Ulladulla .. | 309 | 0.31 | 0.8690 | +29.0° | 1.4752 | 9 Vol. | 13.0 | 43.0 | |
| 8/ 5/1941 | Curl Curl .. | 418 | 0.36 | 0.8690 | +26.66° | 1.4773 | | | | |
| 11/10/1944 | Wattamolla .. | 60 | 0.33 | 0.8799 | +12.27° | 1.4822 | 9.0 Vol. | 11.5 | | |
| 22/10/1947 | Wattamolla .. | 378 | 0.3 | 0.8634 | +17.46° | 1.4779 | 8.5 Vol. | 10.0 | 39.0 | |
| 20/ 7/1948 | Malabar .. | 468 | 0.23 | 0.8733 | +19.5° | 1.4787 | Insol. 10 Vol. | 27.0 | 69.0 | |
| | | | | | | | | | | 3 g. Backeol re- covered after col- lection of oil. |
| | | | | | | | | | | 2.5 g. Backeol re- covered after col- lection of oil. |

EXPERIMENTAL.

A total of 2532 lb. of leaves and terminal branchlets was subjected to distillation in steam, and yielded crude oils possessing physical and chemical constants shown in the table.

The oil obtained from each consignment of foliage was separately investigated, but the results of one only have been selected for publication.

200 ml. of oil (Ulladulla sample, 23/9/40) were distilled at 10 mm., viz. :

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|---------|----------|-----------------------|-------------------------|--------------------|
| 1 | To 60° | 108 | 0.8576 | +37.1° | 1.4718 |
| 2 | 60-65° | 52 | 0.8561 | +28.3° | 1.4737 |
| 3 | 65-70° | 17 | 0.8592 | +19.2° | 1.4761 |
| 4 | Residue | 21 | | | |

The terpene fractions were allowed to stand over metallic sodium prior to fractional distillation through a Widmer column.

Fraction 1 was fractionated over sodium through a Widmer column at 759 mm. pressure.

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|----------|----------|-----------------------|-------------------------|--------------------|
| 5 | To 159° | 6.0 | 0.8557 | +39.2° | 1.4676 |
| 6 | 159-162° | 12.0 | 0.8600 | +39.7° | 1.4682 |
| 7 | 162-164° | 19.5 | 0.8576 | +39.5° | 1.4686 |
| 8 | 164-168° | 27.0 | 0.8606 | +38.6° | 1.4706 |
| 9 | 168-175° | 29.0 | 0.8533 | +34.8° | 1.4736 |

In view of the similarity of physical constants, fractions 5, 6 and 7 were mixed and fractionated at 760 mm., viz. :

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|----------|----------|-----------------------|-------------------------|--------------------|
| 10 | 156-157° | 5.5 | 0.8578 | +40.8° | 1.4677 |
| 11 | 157-159° | 10.0 | 0.8620 | +40.8° | 1.4681 |
| 12 | 159-164° | 6.5 | 0.8610 | +39.5° | 1.4696 |

Fractions 8 and 9 were mixed with fraction 12, and distilled at 760 mm.

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|----------|----------|-----------------------|-------------------------|--------------------|
| 12a | 159-161° | 7.0 | 0.8601 | +39.6° | 1.4691 |
| 13 | 161-162° | 9.5 | 0.8596 | +39.1° | 1.4699 |
| 14 | 162-164° | 13.2 | 0.8590 | +38.8° | 1.4703 |
| 15 | 164-166° | 7.4 | 0.8550 | +38.9° | 1.4711 |
| 16 | 166-168° | 9.4 | 0.8519 | +37.0° | 1.4726 |
| 16a | 168-178° | 11.6 | 0.8528 | +33.2° | 1.4767 |

Fraction 2 was mixed with fractions 16 and 16a and fractionated at 760 mm.

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|------------|----------|-----------------------|-------------------------|--------------------|
| 16b | 169–172° | 10 | 0.8538 | +33.1° | 1.4746 |
| 17 | 172–173° | 13 | 0.8533 | +31.9° | 1.4756 |
| 18 | 173–175° | 7 | 0.8529 | +30.3° | 1.4776 |
| 19 | 175–177.5° | 10 | 0.8510 | +28.4° | 1.4782 |
| 20 | 177.5–178° | 12 | 0.8511 | +25.0° | 1.4786 |
| Residue | | | | | |

Fraction 3 was added to the residue from above distillation, and the mixture fractionated over sodium at 760 mm.

| Fraction. | B.p. | Vol. Ml. | $d_{15}^{15^{\circ}}$ | $\alpha_D^{20^{\circ}}$ | $n_D^{20^{\circ}}$ |
|-----------|----------|----------|-----------------------|-------------------------|--------------------|
| 21 | 178–179° | 7 | 0.8526 | +22.0° | 1.4784 |
| 22 | 179–180° | 3 | 0.8540 | +18.0° | 1.4776 |

Determination of d- α -pinene.

Fractions 10, 11 and 12a on further fractionation yielded a specimen of boiling point 155–159°/760 mm., $d_{15}^{15^{\circ}}$ 0.8610, $\alpha_D^{20^{\circ}}$ +40.8°, $n_D^{20^{\circ}}$ 1.4669. Oxidation with potassium permanganate solution gave a good yield of pinonic acid, m.p. 69–70°: $[\alpha]_D^{20^{\circ}}$ +91.6°; semicarbazone, m.p. 212°.

Fractions 13 and 14 were oxidised with neutral permanganate solution; no crystalline product could be isolated. The semicarbazone prepared from the resinous product had m.p. 212°. A mixed melting point with an authentic specimen of pinonic acid semicarbazone showed no depression.

Examination for Presence of Camphene and β -pinene.

Portions of fractions 2 and 15 respectively were oxidised with alkaline potassium permanganate solution, but products indicative of camphene and β -pinene could not be isolated.

Determination of d-limonene and dl-limonene.

A fraction of b.p. 108°/100 mm. had $d_4^{25^{\circ}}$ 0.8486, $n_D^{25^{\circ}}$ 1.4803, α_D +31°. Four ml. were dissolved in amyl alcohol (4 ml.) and ethyl ether (8 ml.), cooled at –20°, and bromine (4g.) in ether added slowly. After standing for one hour in a bath of acetone and solid carbon dioxide, a yellow precipitate was obtained (0.9 g.). The precipitate was dissolved in chloroform and reprecipitated with ethyl alcohol at room temperature. This treatment was repeated twice, the crystalline bromide having m.p. 125–126°, unchanged in admixture with an authentic sample of dl-limonene tetrabromide; $[\alpha]_D^{20^{\circ}} \pm 0^{\circ}$ in chloroform.

The original chloroform-alcohol filtrate was cooled with acetone and solid carbon dioxide, a precipitate being obtained, m.p. 98–100°, $[\alpha]_D^{20^{\circ}}$ +46°, in chloroform. Purification with chloroform and ethyl alcohol as above yielded crystals of m.p. 103–4°, corresponding to d-limonene tetrabromide.

Determination of γ -terpinene and Cymene.

All fractions boiling above 175°/760 mm., on oxidation with potassium permanganate solution (Penfold, 1925) gave good yields of the erythritol, $C_{10}H_{16}(OH)_4$, m.p. 237–238°, indicative of γ -terpinene.

$\alpha\delta$ -dihydroxy- α -methyl- δ -isopropylapic acid, the oxidation product of α -terpinene, was not isolated.

The unchanged oil, on oxidation with hot potassium permanganate solution, yielded *p*-hydroxyisopropylbenzoic acid, m.p. 156°, which is indicative of *p*-cymene.

Determination of Linalool.

Portion (0.5 ml.) of a fraction of b.p. 74–80°/10 mm., d_4^{25} 0.8621, n_D^{25} 1.4670, α_D +6°, was treated with xenyl carbimide at 100° for one hour. The urethane was isolated and, on repeated recrystallisation from benzene, had m.p. 83–84°.

Sesquiterpenes.

The results of fractionation indicated the presence of sesquiterpenes, but many experiments failed to give crystalline derivatives. Fractions of b.p. 118–123°/10 mm., d_4^{25} 0.9158, n_D^{25} 1.4870, α_D +8° and b.p. 123–132°/10 mm., d_4^{25} 0.9145, n_D^{25} 1.4835, α_D +12°, respectively, gave the characteristic purple colour in glacial acetic acid solution on treatment with bromine vapour.

SUMMARY.

The oil of *Bæckea crenulata* (De Candolle) found growing on the coast of New South Wales and southern Queensland yields from 0.2% to 0.36% of essential oil containing 85% of terpenes, viz. *d*- α -pinene, *d* and *dl*-limonene, γ -terpinene, cymene, together with linalool (10%), bæckeol, sesquiterpenes, and unidentified constituents.

ACKNOWLEDGEMENT.

We are indebted to Mr. K. G. O'Brien, B.Sc., Assistant Chemist, for a complete investigation of the oil obtained from foliage collected at Wattamolla, New South Wales, on October 22, 1947, using the distillation columns described by Lecky and Ewell (1940) and Bower and Cooke (1943), and the technique of distillation based on the methods of Sutherland (1948). This extensive investigation confirmed the work recorded above. Linalool was isolated in a sufficient state of purity to prepare the xenyl urethane. A detailed report of Mr. O'Brien's examination of the oil has been submitted to the University of Sydney as part of a thesis for the M.Sc. degree.

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HEARD ISLAND.

GEOGRAPHY AND GLACIOLOGY.

By A. JAMES LAMBETH, B.Sc.

With two Text-figures.

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GEOGRAPHY.

Early History.

Heard Island appears to have been sighted first by Captain Peter Kemp in 1833 (Mawson, 1935), but it was not until 1853 when it was rediscovered by Captain Heard that the place became generally known. Darwin Rogers, Captain of the *Corinthian*, was the first to land. The island was apparently visited from time to time by sealers but prior to 1947 only four scientific expeditions had called there.

The *Challenger* Expedition (1885) arrived on 5th February, 1873, and a party spent several hours ashore at Corinthian Bay. The German *Gauss* Expedition (Drygalski, 1908) in February, 1902, landed in the vicinity of Atlas Cove. Aubert de la Rue (1929) in 1929 stayed eight days at Atlas Cove, living in a hut erected there by the British Admiralty some years before. In November of the same year the B.A.N.Z. Antarctic Expedition (Mawson, 1932) under the leadership of Sir Douglas Mawson stayed several days at the same place.

On 11th December, 1947, the Australian National Antarctic Research Expedition established a base camp on Rogers Head adjacent to Atlas Cove.

Position of the Island.

Heard Island lies in 73° 30' E. longitude at 53° 05' S. latitude, almost halfway between Australia and South Africa. Kerguelen's Land lies about 200 miles to the north-north-west, and the Antarctic Continent—MacRobertson Land—is approximately 1100 miles to the south. The island is approximately 28 miles long and 12 miles broad, the longer axis lying in a N.W.-S.E. direction.

It is the largest member of the McDonald Group, and McDonald Island lies about 27 miles away to the north-west.

The surrounding seas abound with rocks and reefs ; notable are the Shag Islands and Wakefield Reef, situated respectively a few miles off the central eastern and western coasts of Heard Island.

Description.

Heard Island is almost circular in plan, but is modified by two opposing appendages. The coastline is precipitous ; rock cliffs and the vertical ice fronts of glaciers alternate. These cliffs sweep rapidly upwards to form the mountain mass known as Big Ben Range, which is almost completely snow and ice covered. Several minor peaks are located here, e.g. Fremantle Peak (7800 ft.) and Campbell Peak (7923 ft.), whilst the culminating peak is Mt. Mawson (9005 ft.). This cone-shaped peak has a crater at the top and rises about 1000 ft. above the semi-plateau-like top of Big Ben Range.

Cape Laurens is an imposing mass of small dimensions joined to the island by a narrow tract of low land. The coast is composed of rock cliffs varying from 100 ft. to 1000 ft. in height. The northernmost extremity is Red Island, an extinct volcano (309 ft.), joined through a spit-like junction, thus forming a tied island. The summits of Cape Laurens are snow fields and ice sheets, and the spine-like Mt. Anzac is the highest point (2347 ft.). Lesser peaks are Mt. Dixon (2316 ft.) and Mt. Olsen (2080 ft.).

The south-eastern end of the island is a spit-like structure about five miles long, which swings away seaward after the manner of a tail. This area is low lying and contains a shallow lake.

The coastline of Heard Island shows very little relief, consequently bays and inlets are poorly developed. Atlas Cove is the best and is a fjord-like structure. Corinthian Bay is a large semi-circular bay, as is also South West Bay. Beaches occur ; notable are Fairchild Beach and Long Beach, the low land at Atlas Cove, and the boulder beaches of Spit Point.

The island is of volcanic origin and the grandeur and ruggedness are due to the height and mass of Big Ben Range and Mt. Mawson.

The map reproduced here (Fig. 1) is after that produced by the Expedition during 1948.

GLACIOLOGY.

Snow Line.

Fully ninety per cent. of the area of Heard Island is covered with ice and snow throughout the year.

The snow line varies according to the season. In December, 1947, it was at 1000 ft., and remained stationary until the end of April, 1948, when it commenced to descend. By the 1st July, 1948, it had reached sea-level, where it remained until 1st September. At this stage it commenced to retreat and was at approximately 200 ft. at the end of that month. In the middle of November the snow line was at 500 ft., from which it retreated to 1000 ft., reaching this level at the end of the first week in December, 1948.

There was little difference in the level between northerly and southerly aspects.

Glaciers.

Glaciers on Heard Island may be discussed under two headings : those situated on Cape Laurens and those on the island proper.

Those situated on Cape Laurens are small in size, due to the small area and low altitude of the collecting grounds. Mt. Dixon is covered by a continuous ice sheet, which descends to approximately 600 ft. Between Mt. Dixon and

Anzac Peak two glaciers rise, one flowing north, the other south. These descend to approximately 500 ft., where they ablate amongst small piles of moraine.

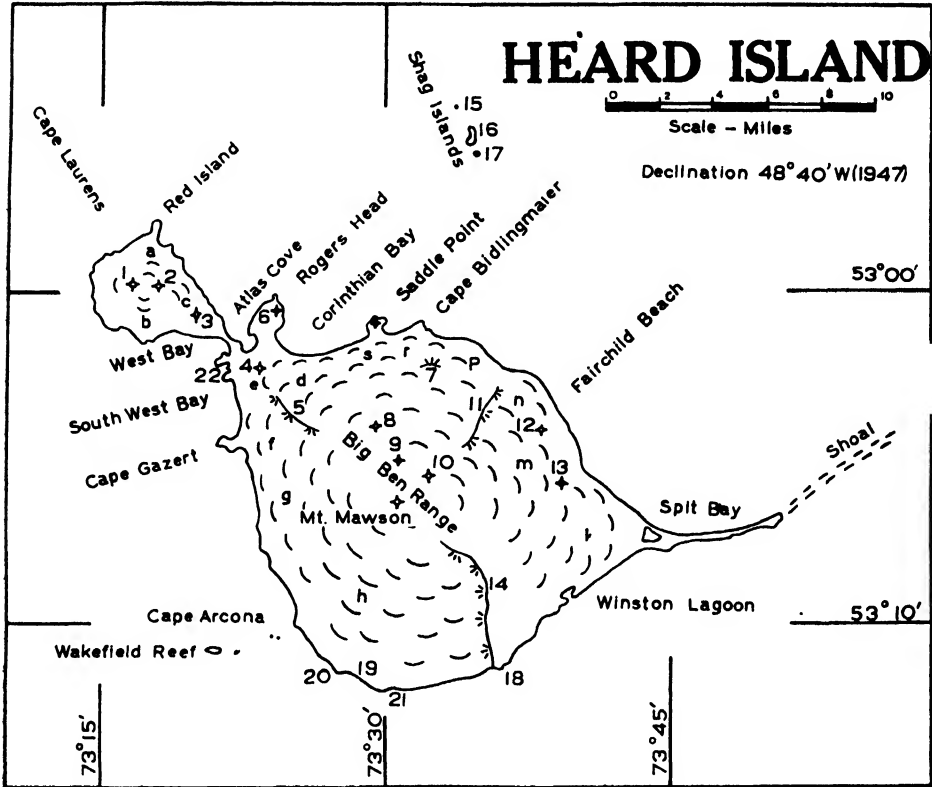


Fig. 1.—Key to Map of Heard Island. Minor Geographical Features.

| | |
|-------------------------|----------|
| 1. Mt. Dixon .. | 2316 ft. |
| 2. Anzac Peak .. | 2347 ft. |
| 3. Mt. Olsen .. | 2080 ft. |
| 4. Mt. Drygalski .. | 690 ft. |
| 5. North-West Cornice | |
| 6. Corinthian Head .. | 592 ft. |
| 7. Melbourne Bluff .. | 1265 ft. |
| 8. Little Matterhorn .. | 4856 ft. |
| 9. Fremantle Peak .. | 7800 ft. |
| 10. Campbell Peak .. | 7923 ft. |
| 11. North Barrier | |
| 12. Round Hill .. | 1252 ft. |
| 13. Scarlet Hill .. | 1346 ft. |
| 14. South Barrier | |
| 15. Sail Rock .. | 56 ft. |
| 16. Shag Island .. | 301 ft. |
| 17. Drury Rock .. | 122 ft. |
| 18. Cape Lambeth .. | 700 ft. |
| 19. Long Beach | |
| 20. Cape Labuan .. | 130 ft. |
| 21. Cape Lavett | |
| 22. Cave Bay | |

Glaciers.

| |
|-------------------------|
| a. Unnamed. |
| b. " |
| c. Jacka Glacier. |
| d. Baudissin Glacier. |
| e. Schmidt Glacier. |
| f. Vahsel Glacier. |
| g. Abbottsmith Glacier. |
| h. Gotley Glacier. |
| k. Unnamed. |
| m. " |
| n. Compton Glacier. |
| p. Unnamed. |
| r. " |
| s. Challenger Glacier. |

The eastern wall of these glaciers is an almost vertical cliff, which is a structural geological feature, a fault scarp.

Between Mt. Olsen and Anzac Peak and flowing east towards Atlas Cove is the Jacka Glacier. This is the largest glacier of Cape Laurens and was undoubtedly a hanging glacier to the former and now non-existent glacier flowing northwards down Atlas Cove. This older glacier appears to have been of the valley type with Cape Laurens forming the western wall. At the top of the cliffs here is a typical alb formation, indicating the upper limit of the glacier. As the course of this old glacier is intersected by a relatively recent geological fault of large throw, it is evident that the retreat was caused by the lowering of the collecting grounds.

The glaciers situated on the island proper rise from the heights of Big Ben Range. Many reach the sea, but occasionally the front is land-based. Whilst all of them show the effect of plucking action of ice on the underlying rock, generally walls and sides of rock are wanting. It is frequently difficult to determine the boundaries. Often these are low discontinuous mounds of highly crevassed ice. The glaciers lack well defined cirques.

The course of the typical glacier is interesting. Rising on Big Ben Range, the ice flows over the rim of the plateau through areas of intense crevassing. The ice then enters a structure resembling an avalanche-shute, the top of which is marked by a rock cliff normal to the course. Re-formation takes place between two lateral rock walls which are thickly encrusted with ice. Pinnacles and aiguilles are common on these walls. The surface of the glacier now becomes convex in profile and the lateral walls become insignificant. One glacier may contain several of these amphitheatre-like structures. That these are not cirques is indicated by the fact that the material entering is already blue ice.

The glaciers therefore resemble ice sheets modified by plucking action at certain places. Consequently they are to be considered as belonging to the Spitzbergen type.

Although many glaciers are sea-based, none is actually afloat. It was considered that the ice foot was not far vertically below sea-level.

The total depth of ice is uncertain, but measurements taken on the fronts of glaciers indicate that probably 150 ft. may be the upper limit. For example the front of the Baudissin Glacier was measured at 110 ft. in August, 1948, whilst the front of the Vahsel Glacier was 125 ft. thick in the same month. Although the fronts are thinner than the main masses due to ablation, the observations were taken when ablation was at a minimum.

Retreat of Glaciers.

Recent retreat of glaciers and evidence of loss of ice cover in the Antarctic have been reported by Warner (1945) and Knowles (1945). The former has evidence to show the loss of "several hundred vertical feet" of ice.

An indication of a similar recent diminution on Heard Island is afforded by the terminal and lateral moraines of the Vahsel Glacier. The front of this glacier abuts in part on to Cape Gazert, a small headland of bedded lavas. Overlying these lavas are two terminal moraines, as indicated in Figure 1. The terminal moraine situated immediately at the glacier front has an altitude of approximately 125 ft., whilst a short distance away is an older and more consolidated moraine of altitude 320 ft. approximately. The evidence indicates a loss of at least 200 ft. vertical thickness of ice but little horizontal retreat along the glacial path. The lateral moraine of the same glacier shows a similar diminution, as shown in Fig. 2. The older moraine here has an altitude of 300 ft., which is approximately 220 ft. higher than the more recent moraine.

Ablation of Glaciers.

Dissipation of ice takes place by melting, by the action of the sea, or by avalanching.

Melting takes place through the action of the sun, wind and rain. These agencies are seldom significant above 1000 ft. During November, 1948, an ablatograph was maintained on the north slopes of the Baudissin Glacier. The

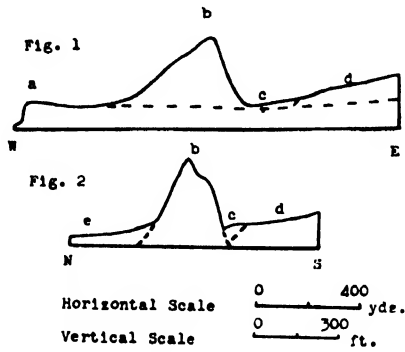


Fig. 1 above. Section at Cape Gazert, indicating retreat of the Vahsel Glacier.
Fig. 2 above. Section near Erratic Point. The lateral moraine of the Vahsel Glacier, indicating retreat.

- a. Bedded lavas.
- b. Old moraine.
- c. Active moraine.
- d. Vahsel Glacier.
- e. Redistributed moraine.

Datum lines are at sea-level.

apparatus was at 125 ft. above sea-level, and the record concerns the ablation of clear blue ice. In general the ablation was greater during the hours of daylight than during darkness, and rain, however cold, was more effective than sunshine, which in turn was more effective than wind. The following condensed record illustrates these points.

| | Typical Period of Sunshine. Decrease/Hour. Average, Inches. | Typical Period of Light Fairly Constant Rain. Decrease/Hour. Average, Inches. | Typical Period of Wind. Overcast. Decrease/Hour. Average, Inches. |
|---------------------------|--|---|---|
| 12 p.m. to 3 a.m. | 0.00 | — | 0.02 |
| 3 a.m. „ 6 a.m. | 0.00 | — | 0.00 |
| 6 a.m. „ 9 a.m. | 0.03 | 0.15 | 0.00 |
| 9 a.m. „ 12 noon | 0.05 | 0.14 | 0.02 |
| 12 noon „ 3 p.m. | 0.12 | 0.20 | 0.00 |
| 3 p.m. „ 6 p.m. | 0.06 | 0.06 | 0.00 |
| 6 p.m. „ 9 p.m. | 0.00 | 0.03 | 0.00 |
| 9 p.m. „ 12 p.m. | 0.00 | — | 0.00 |

During the entire month ablation at this station from all causes averaged 0.02 in. per hour approximately.

The melt water finds its way into the ice through crevasses, sinks and crevices, emerging as a torrent through a circular hole at the front of the glacier. In hanging glaciers this water issues as a waterfall, but in the case of sea-based types a discoloured stream enters the sea. In February, 1948, the glacial stream from the Challenger Glacier was discernible two and a half miles to seaward, whilst in February, 1949, sea water five miles off the south-eastern end

of the island was strongly discoloured. In this case the effect is due to a coalescence of the streams as they are swept eastwards round the flanks of the island by the westerly drift of wind and sea.

The sea is effective in the dissipation of glacial ice. The action is twofold. The pounding of the waves causes undercutting at the foot, resulting in avalanching of the front. Secondly, the deposition of salt spray on the lower level ice causes deterioration of the surface and an opening of cracks and crevasses, which later become lines of weakness along which the avalanches shear off.

Avalanches of this kind vary in size. On the Baudissin Glacier, where the front averaged 100 ft. high, the falls were about 100 yards in length. The ice which falls into the sea is well fragmented, so that large bergs do not result.

Movement of Glaciers.

Observations were carried out on the Baudissin Glacier between the months September to December, 1948. The observation poles were at an altitude of 300 ft. approximately, about half a mile inland. The maximum movement recorded was at the centre, where a movement averaging one foot per day was recorded for the period 11th September to 20th October. In the period 20th October to 8th December this had increased to a daily average of three feet.

Types of Moraines.

Land-based glaciers end in a terminal moraine; in sea-based types shallow water extends offshore for some distance. Lateral moraines are usually small in size, due to the lack of well-defined walls. The lateral moraine on the north side of the Vahsel Glacier is the largest on the island. It ends in the geographical feature Erratic Point, which contains the largest erratics encountered. Several of these are of the order of 1000 tons. The unusual development of this moraine is due to the high, cliff-like wall, the North West Cornice, which contains the glacier in the lower reaches.

The material deposited ranges from rock flour to boulders of the size mentioned above. Large boulders are rare, the bulk of the material being less than three feet in diameter. Whereas the bulk of material in lateral and medial moraines is angular, the material of the terminal moraines contains a large proportion of rounded and sub-rounded débris. Rounded débris weathers out of solid ice high up on the glacial fronts, as well as issuing with melt water from various tunnels. Scratched and soled pebbles are uncommon, but are more abundant in lateral moraines than in terminal moraines.

Medial moraines are few and small in size; noteworthy are the two medial moraines of the Compton Glacier. Knob and kettle-structure on a small scale occurs in the moraine of the glacier confronting Saddle Point.

An unusual feature is the large redistributed moraine of Atlas Cove. This has been derived from waste of the Baudissin, Schmidt and Vahsel glaciers, which converge at this point, and possibly in part from the old, now non-existent, glacier flowing down Atlas Cove. The area is flat with a maximum elevation of 60 ft. The débris has been modified by the action of wind and waves and also by slumping, so that it assumes the nature of a plain.

Evidence of bodily shift of these sediments was provided by a stake in the sediments between Corinthian Bay and Mt. Drygalski. This stake moved fifteen feet in eleven months towards Corinthian Bay, thus indicating a spreading by slumping towards deep water. When under the influence of the sea the detrital material becomes subject to westerly drift and is worked round the flanks of the island to the south-east end, where it is deposited in the lee. This has caused the long thin tail-like spit to be built up.

Freezing of Bodies of Water.

Freezing of the sea was noted on 30th July, 1948, and between then and 14th October freezing occurred on eighteen occasions. This was confined to relatively quiet bodies of sea water and took the form of pancakes of ice and slush. The freezing occurred most commonly on clear nights. The solid phase separated at a temperature of 28.6° F., and was fresh. The most severe case of freezing of the sea was noted on 15th September, 1948.

Snow Types.

Snow falls at sea-level throughout the year; however that which falls during summer is quickly dissipated and cold rain is more common. Falls during the winter build up large drifts. An analysis of observations on snow seen to fall about the base camp during the period 1st September to 1st December, 1948, showed that almost 90 per cent. could be classified as either stars, spicules and rods, or frozen rain, the proportions being nearly equal.

Twice during this period snow was observed to accumulate with a preferred orientation. On these occasions the factors were (a) the shape of the grains, and (b) the influence of the wind. Both times the major axis of the grains was very much longer than the two minor axes, so that the acicular type grains lodged parallel to the surface of the ground and then orientated themselves parallel to the direction of the wind.

SUMMARY.

Heard Island is a small precipitous volcanic island situated within the McDonald Group at 53° south latitude in the Indian Ocean. The climate at sea-level is sub-antarctic. The snow-line is at 1000 ft. during summer but descends to sea-level in winter. During this latter period the sea was observed to freeze. The island is almost completely glaciated and the depth of ice-cover is in excess of 100 ft., although there is evidence to show that this depth was formerly much greater. Descriptions of moraines and glaciers are given and there are also notes on the ablation of ice and the types of snow.

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6 MAY 1953

RANK VARIATION IN THE CENTRAL EASTERN COALFIELDS OF NEW SOUTH WALES.

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With Plate III and two text-figures.

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INTRODUCTION.

Considerable variation has long been recognised in the nature and properties of coal in the different coalfields situated around the margin of the Permian Coal Basin in Central Eastern New South Wales. It is well known, for example, that coals in the South Coast Field are very friable and "dusty" compared with other fields and that they are characterized by low moisture contents, high carbon contents, low volatile yields, and excellent coking properties. Coals from the Northern, South-western and Western Fields are less friable, contain more moisture and less carbon, give higher volatile yields, and, with some important exceptions in the Newcastle-Swansea area, are more suitable for gas-making and steam-raising than coke production. In the Ulan-Baerami Field, situated between Mudgee and Muswellbrook, the seams are particularly firm, with relatively high moisture contents, low carbon contents, high volatile yields and very poor coking properties.

Such variations in the nature and properties of coal are due largely to rank differences, or different degrees of metamorphic development. Type differences play only a minor part in variations of properties as all the coals concerned are of the same general type. The investigation recorded in this paper was carried out with the object of obtaining quantitative data bearing on regional variation of rank throughout the Upper Coal Measures of the Central Eastern Coal Basin and on the metamorphic history of the area. Results also have some bearing on the relationship between different chemical and physical rank indices.

The coal-bearing strata of the Newcastle stage of the Upper Coal Measures are continuous throughout all the coalfields. The Tomago Measures outcrop only in the Northern Coalfield but the coal is generally similar in rank and type to coal of the Newcastle Measures in the same section of the coalfield, and for the purpose of the present paper coals of the two stages of the Upper Coal Measures are considered together. The Greta or Lower Coal Measures also outcrop on the Northern Coalfield but they contain coal of a somewhat specialised type, which differs from coal of the Upper Coal Measures in nature and condition of original plant material. In view of this and the substantial differences in stratigraphical position, the Greta coal is not included with the Upper Coal Measure coals in considering regional rank variation, but the relation of its rank to other Permian coals is discussed separately. The Permian coals of the Werris Creek-Curlewis-Gunnedah Coalfields are not included in the present work as the coal-measure strata in that area form part of the Great Artesian Basin, and the rank of the coal is not directly related to the tectonic history of the Central Eastern Coal Basin.

Vitrain, which is coalified wood and bark, was used for the study of rank variation so as to eliminate, as far as possible, the influence of varying proportions of "banded constituents". Blocks of coal containing well-developed vitrain bands were obtained from 48 collieries and fresh exposures of coal seams in the different coalfields. In the case of each locality involving the area of a colliery workings, or a fresh exposure of a seam in a railway tunnel or cutting, pure vitrain was separated by hand from at least five or six different bands. Aggregate samples so obtained were analysed to provide average results for vitrain in each locality and to eliminate to some extent variations inherent in the nature of the vitrains. The materials were crushed, sieved and water saturated, then acid washed to remove as much adherent mineral matter as possible. After complete removal of acid by prolonged soaking in water and repeated washing, the samples were used for determination of carbon and hydrogen by ultimate analysis; volatiles, fixed carbon and ash by proximate analysis; and maximum inherent moisture by "controlled vaporization of adherent moisture" (Dulhunty, 1947*a*). Results of the chemical and physical determinations for the vitrains are recorded in Table I.

The ultimate and proximate analyses provide two sets of chemical-rank indices. Values for maximum inherent moisture provide an index of physical rank. The expression "physical rank" is used in relation to progressive changes in the physical state of coal as it matures under natural metamorphism (Dulhunty, 1947*b* and 1948). It is concerned largely with the degree of physical development of micelle or ultra-fine structure of the coal, and it has been shown that this is closely related to values for maximum inherent moisture (Dulhunty, 1947*b*; Hinder, 1949).

RELATIONS BETWEEN DIFFERENT RANK INDICES

Relations between results of proximate and ultimate analyses as chemical rank indices and maximum inherent moisture as a physical rank index were examined by plotting different properties against each other. In Fig. 1 carbon was plotted against fixed carbon for each of the vitrains analysed. The points fall in a relatively wide zone which rises across the diagram from left to right. From the width of the zone it is evident that they are not closely related. Vitrains with any given carbon content may vary in fixed carbon over a range of about 10 per cent. and those of any given yield of fixed carbon may vary in carbon by about 8 per cent. The points fall towards the upper or lower limits of the zone, or the carbon-fixed carbon ratio deviates from the mean, without any apparent reason. The deviation is not related to geographical position or stratigraphical horizons in the coalfields, nor is it related to physical rank of the vitrains, or to the carbon-fixed carbon ratio of the coal seams in which the vitrains occur. It may, however, be related to other factors, such as petrological constitution, which remained to be investigated. It is also possible that deviation of the carbon-fixed carbon ratio may be related to some variable factor in the chemical constitution of the coal substance. In view of this, and the fact that fixed carbon values vary with the conditions of determination, it would seem that carbon content probably represents a more reliable and significant index of chemical rank than fixed carbon. It is evident, however, that fixed carbon may be regarded as a general indication of rank within the limits of variation corresponding to the width of the zone in Fig. 1.

The relations between physical and chemical rank have been studied by plotting values for maximum inherent moisture against carbon of vitrains in all stages of metamorphic development (Dulhunty, 1948). Results showed a zonal relationship with a well-defined maximum at about 68 per cent. carbon and a minimum at about 89 per cent. carbon. The width of the zone, which varies considerably with rank (as illustrated in the above references), is regarded

TABLE I.
Results of Analyses of Vitrain Samples.

| Coalfield. | Locality. | Seam. | C.S. No. | Percentage Ash-Free Dry Coal. | | Ash Percentage Dry Coal. | M.I.M. Percentage Ash-Free Dry Coal. |
|------------------|----------------|-------|-------------------|-------------------------------------|------|--------------------------------|---|
| | | | | C. | F.C. | | |
| South Coast | Sydney .. | No. 1 | 30 | 88.3 | 77.3 | 1.1 | 3.2 |
| | Helensburgh .. | No. 1 | 312 | 88.0 | 76.0 | 0.9 | 1.8 |
| | Clifton .. | No. 1 | 313 | 88.8 | 75.4 | 0.9 | 1.8 |
| | Austinmer .. | No. 1 | 314 | 88.9 | 73.0 | 0.8 | 2.3 |
| | Bulli | No. 1 | 445 | 89.7 | 72.3 | 1.7 | 1.9 |
| | Bellambi .. | No. 2 | 356 | 89.7 | 73.6 | 1.1 | 2.3 |
| | Corrimal .. | No. 1 | 394 | 87.3 | 73.5 | 0.6 | 2.1 |
| | Keiraville .. | No. 1 | 444 | 88.3 | 70.4 | 3.7 | 2.0 |
| | Unanderra .. | No. 3 | 439 | 88.4 | 73.5 | 3.2 | 1.9 |
| | Unanderra .. | No. 2 | 352-88 | 88.1 | 71.5 | 0.5 | 2.5 |
| | Dapto | No. 3 | 443 | 88.1 | 71.4 | 2.6 | 2.0 |
| South Western | Berrima .. | No. 3 | 347-8 | 84.8 | 67.8 | 4.7 | 4.1 |
| | Nattai .. | No. 3 | 681 | 84.9 | 66.8 | 2.2 | 3.0 |
| Western | Katoomba .. | No. 1 | 671 | 82.4 | 67.8 | 2.9 | 3.0 |
| | Lithgow .. | No. 7 | 446 | 84.6 | 68.0 | 2.6 | 7.4 |
| | Lithgow .. | No. 7 | 362 | 83.0 | 66.9 | 0.8 | 5.0 |
| | Lidsdale .. | No. 6 | 360 | 85.6 | 64.7 | 2.2 | 7.7 |
| | Cullen Bullen | No. 6 | 366-7 | 82.4 | 63.8 | 1.2 | 6.0 |
| | Cullen Bullen | No. 6 | 430 | 81.2 | 63.4 | 1.4 | 6.0 |
| | Glen Davis .. | No. 1 | 667 | 83.5 | 67.7 | 4.2 | 4.1 |
| | Charbon .. | No. 7 | 373 | 83.7 | 66.5 | 0.8 | 8.3 |
| | Kandos .. | No. 7 | 181 | 80.8 | 64.5 | 2.1 | 6.4 |
| Ulan- Baerami | Ulan | No. 7 | 667 | 78.5 | 62.0 | 1.6 | 9.5 |
| | Wollar .. | No. 6 | 651 653 656 | 82.4 | 63.5 | 1.6 | 11.3 |
| | Kerrabee .. | No. 6 | 666 | 78.3 | 65.6 | 2.5 | 10.9 |
| | Kerrabee .. | No. 6 | 673 | 80.0 | 66.7 | 1.9 | 11.8 |
| | Baerami .. | No. 3 | 672 | 79.2 | 66.5 | 0.6 | 9.0 |

TABLE I.—Continued.
Results of Analyses of Vitrain Samples.—Continued.

| Coalfield. | Locality. | Seam. | C.S. No. | Percentage Ash-Free Dry Coal. | | Ash Percentage Dry Coal. | M.I.M. Percentage Ash-Free Dry Coal. |
|------------|-----------------------|--------------------|----------------|-------------------------------------|------|--------------------------------|---|
| | | | | C. | F.C. | | |
| Northern | Muswellbrook . . | Tomago Measures | 675 | 85.0 | 70.4 | 1.9 | 4.3 |
| | Liddell . . | Tomago Measures | 174 | 81.0 | 61.6 | 3.1 | 4.0 |
| | Rix Creek . . | Tomago Measures | 447-52 | 81.8 | 62.6 | 2.0 | 4.6 |
| | Rix Creek . . | Tomago Measures | 172 | 80.9 | 63.6 | 4.4 | 6.0 |
| | East Maitland | Tomago Measures | 363 | 79.4 | 64.4 | 0.7 | 4.9 |
| | East Maitland | Tomago Measures | 364 | 81.7 | 64.7 | 2.1 | 4.7 |
| | West Wallsend | Tomago Measures | 169 | 81.3 | 66.1 | 1.8 | 5.6 |
| | Adamstown . . | Victoria Tunnel | 353 | 83.4 | 62.9 | 5.1 | 3.9 |
| | Whitebridge . . | Borehole | 377 | 82.2 | 64.0 | 3.0 | 4.4 |
| | Whitebridge . . | Victoria Tunnel | 396 | 82.3 | 64.0 | 2.5 | 4.6 |
| | Redhead . . | Victoria Tunnel | 458 | 83.7 | 64.3 | 3.4 | 4.0 |
| | Belmont . . | Borehole | 404 } 433 } | 84.7 | 65.8 | 0.5 | 3.9 |
| | Belmont . . | Victoria Tunnel | 405 } 435 } | 82.8 | 66.1 | 2.2 | 4.4 |
| | Belmont . . | Great Northern | 459 | 83.4 | 63.7 | 2.4 | 4.8 |
| | Swansea . . | Wallarrah | 461 | 79.8 | 64.2 | 5.6 | 6.1 |
| | Catherine Hill Bay | Wallarrah | 460 | 84.05 | 67.8 | 1.7 | 5.8 |
| Greta | Cessnock . . | Greta | 310 | 80.8 | 62.2 | 1.6 | 4.0 |
| | Kearsley . . | Greta | 408-9 | 81.6 | 62.9 | 2.2 | 3.9 |
| | Kearsley . . | Greta | 401 } 403 } | 81.8 | 65.8 | 1.3 | 4.4 |
| | Pelaw Main | Greta | 390 } 393 } | 82.6 | 62.9 | 1.3 | 4.0 |
| | Muswellbrook . . | Greta | 412 } 413 } | 80.7 | 63.8 | 0.6 | 8.1 |

as an indication of the extent to which the two forms of rank may become separated in degree of advancement during metamorphic development. If a point falls towards the lower limits of the zone, between 68 and 89 per cent. carbon, it means that its physical rank is considerably in advance of its chemical rank. Conversely, if a point falls near the top of the zone, between the same limits of carbon, its chemical rank is in advance of its physical rank.

The relationship between chemical and physical rank for vitrains of the Central Eastern Coal Basin is illustrated in Fig. 2. Owing to the limited range in rank of the vitrains concerned (78-90 per cent. carbon), this diagram represents only that portion of the zone where it approaches the minimum at 89 per cent. carbon. It will be noted in Fig. 2 that there is a distinct crowding of points on

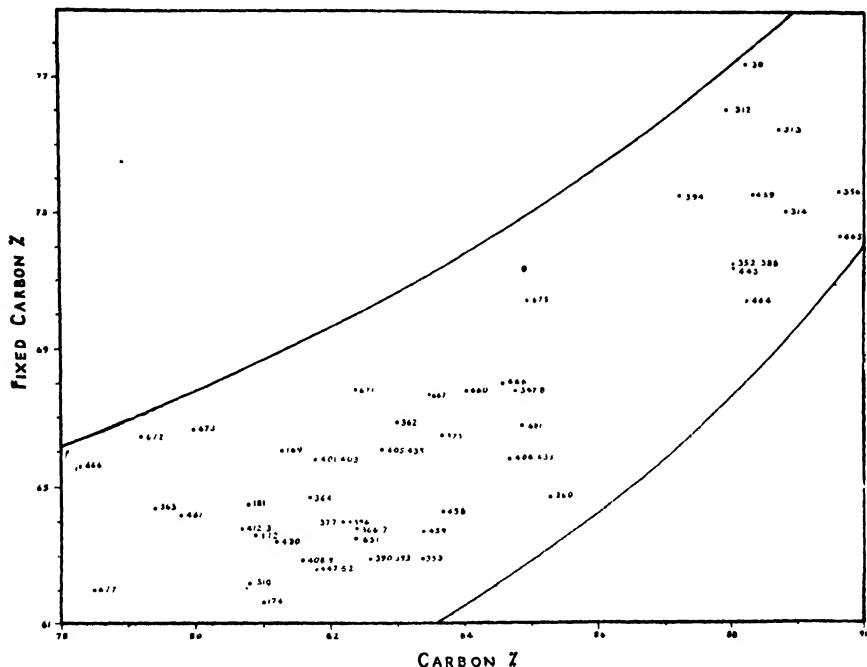


Fig. 1.—Relations between Carbon and Fixed Carbon for Aggregate Vitrain Samples.

the lower side of the zone. From this it may be inferred that vitrains from the majority of localities are considerably more advanced in physical rank than chemical rank. The few vitrains which fall towards the upper side of the zone are all from the western margin of the coal basin in the Western and Ulan-Baerami Coalfields, suggesting that these were the only areas in which conditions of metamorphism were such as to advance chemical rank more than physical rank. These points which fall close to the lower limits of the zone are all from the Maitland-Liddell-Cessnock section of the Northern Coalfield, suggesting the existence of conditions capable of advancing physical rank more than chemical rank. Such results may have an important bearing on prevailing conditions of metamorphism in different parts of the coal basin and on the tectonic history of the coal measures when more is known about the relative influence of various metamorphic factors in the process of coalification.

REGIONAL VARIATION OF CHEMICAL AND PHYSICAL RANK.

In the study of regional variation of physical and chemical rank in the Upper Coal Measures maximum inherent moisture and carbon were used

respectively as indices of the two forms of rank. The area of the Central Eastern Coal Basin and its arbitrary subdivision into coalfields, is shown on the accompanying map (Plate III). Localities from which vitrains were selected for the investigation are indicated by small crosses numbered with the serial numbers of vitrain samples in Table I, which supplies detailed chemical and physical data. The values for carbon and maximum inherent moisture shown on the map represent average results for vitrain in the vicinity of the places where the figures appear. In each the average was obtained for all vitrains in an area extending about halfway to the nearest place where another average is shown. Average results of this kind were placed on the map as the printing of individual results produced too much confusion, and because small local variations in properties tended to obscure the general picture of regional variation. "Isocarbs" or lines indicating distribution of carbon content were drawn on the map at intervals of 2 per cent. from 78 to 90 per cent. carbon. Similar lines

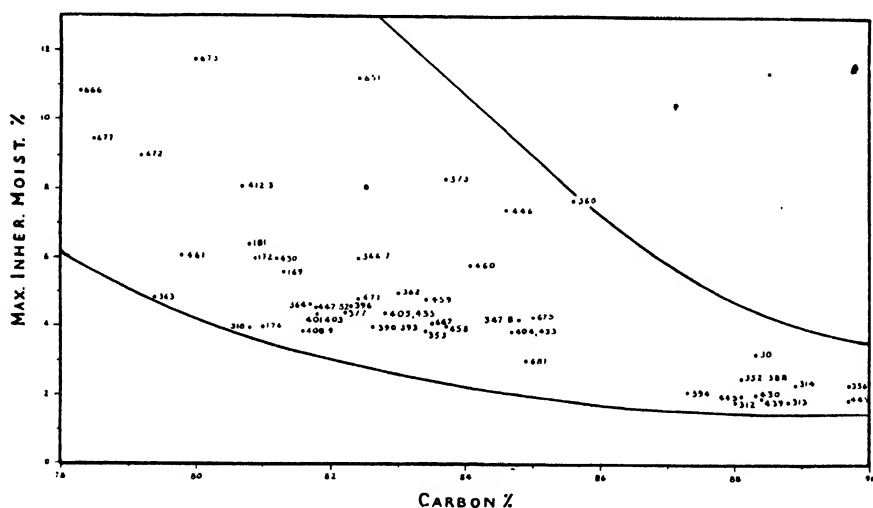


Fig. 2.—Relations between Carbon and Maximum Inherent Moisture for Aggregate Vitrain Samples.

were drawn for maximum inherent moisture at intervals of 1 per cent. from 2 to 11 per cent. These lines have been termed "isomoists" for the purpose of the present paper.

Distribution of chemical rank illustrated by the isocarbs shows a general centre of metamorphism or maximum rank advancement in the vicinity of the South Coast Coalfield. Rank decreases rapidly towards the South-western Coalfield and somewhat less rapidly in the direction of the Northern Coalfield, whilst in a north-westerly direction it decreases very slowly through the centre of the coal basin. Rank also decreases through both the Western and Northern Coalfields towards the Ulan-Baerami Field, where the coals of lowest rank are situated. The centre of high rank on the South Coast is situated towards the southern margin of the coal basin and does not coincide with the general centre of sedimentation or the structural centre of the basin. Beyond the influence of the high rank centre in the south, the isocarbs tend to follow the original shore lines of coal-measure sedimentation. They also appear to be somewhat crowded along the marginal areas leaving a large area in the central region where rank variation is only slight.

Physical rank variation illustrated by the isomoists follows the same general trends as the distribution of chemical rank. A centre of high physical rank with

low moisture values is situated in the vicinity of the South Coast Coalfield and values increase as rank becomes lower through the Western and Northern Coalfields towards the Ulan-Baerami area, where the highest moisture values occur in coals of the lowest rank. As in the case of chemical rank there is a relatively rapid decrease in physical rank, or crowding of isochoists, along the marginal areas of the basin and variation is slight in the central region.

Although the two forms of rank show the same general distribution in relation to the coal basin there are some small but very significant differences in rate of variation. In the Western and Ulan-Baerami Coalfields the isochoists are far more crowded than the isocarbs indicating that physical rank decreases more rapidly than chemical rank. This can be correlated with the conclusion, based on the positions of vitrains in the zonal relationship between moisture and carbon (Fig. 2), that in the Western and Ulan-Baerami Coalfields conditions of metamorphism were such as to advance chemical rank more than physical rank. If chemical rank is more advanced than physical rank then the rate of change in physical rank on passing towards the Ulan-Baerami Field, will be greater than change in chemical rank. This is so as the isochoists are more crowded than the isocarbs in the Ulan-Baerami Coalfield. Similarly it was concluded in discussing Fig. 2 that physical rank was more advanced than chemical rank in parts of the Northern Coalfield, and it is evident from the map that isocarbs are somewhat more crowded than isochoists in that area. Another example of correlation between rank distribution and the positions of vitrains on the moisture-carbon diagram can be seen in the South-western Coalfield. In this area isocarbs are more crowded than isochoists and the vitrains fall towards the lower side of the zone in Fig. 2.

From the foregoing discussion and results it would seem to follow that features such as relative crowding of isocarbs and isochoists or the different rates at which physical and chemical rank vary from place to place, and the crossing of isocarbs and isochoists must be related to differences in metamorphic conditions or the predominance of different metamorphic factors which have existed in various regions of the coal basin. As stated earlier, when more is known about the relative influence of different metamorphic factors during coalification it is highly probable that much information about the geological history of coal measures will be revealed by relations between the distribution of physical and chemical rank, as illustrated by isocarbs and isochoists in Plate III.

STRATIGRAPHICAL VARIATION IN RANK.

In many coalfields of the world the coal seams exhibit a definite increase in rank with depth from the surface. This is generally attributed to increase in pressure and temperature with depth. In the Central Eastern Coal Basin of New South Wales there is a general tendency for isocarbs and isochoists to follow the original shore lines of deposition along the western and north-eastern sides of the basin where rank increases on passing towards the central regions. This is probably due to increases in depth of cover, but the principal trends in rank variation are not related to depth of burial or thickness of the coal measures. For example, rank decreases progressively from 84 per cent. carbon to 78 per cent. carbon in a northerly direction along the western margin of the basin. The centre of high rank on the South Coast is situated towards the southern margin of the basin and cannot be correlated with either depth of burial or thickness of coal measures. The highest and lowest rank coals occur in the South Coast and Ulan-Baerami Coalfields respectively although depth of burial in each case, and physiographic histories of the two areas, appear to have been much the same.

Vitrain bands occur in the topmost beds of Triassic sandstone near Sydney. The rank of the Triassic vitrains (about 86 per cent. carbon) is almost as high

as that of Permian vitrains (88 per cent. carbon), which occur some 3000 ft. deeper in the same area. Also, the rank of the Triassic vitrain is much higher than the Permian vitrains along the western and north-western sides of the basin. The strata are practically undisturbed by folding or faulting in any of these areas. It is possible that the high carbon contents of the Triassic vitrains near Sydney may be due to coalification in a sandstone environment rather than the general coal-measure environment in which the underlying Permian vitrains were formed. If, however, their high carbon contents resulted from regional metamorphic conditions, which appears likely, then some factors other than depth must have produced the high-rank coals between Sydney and Wollongong and those factors would appear to have operated in post-Triassic time. The large number of igneous sills and dykes injected into the coal measures and underlying marine beds along the South Coast may have elevated the general temperature of the strata sufficiently to produce coals of higher rank than in any other part of the coal basin. In general, however, it appears that rank variation in the Central Eastern Coal Basin is not a simple consequence of depth of burial, and cannot be related to folding or other tectonic disturbances in the coal measures.

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In conclusion the authors wish to express appreciation of generous assistance given by Colliery Proprietors and Managers in obtaining coal samples for the investigation. They also wish to acknowledge assistance given by the Combined Colliery Proprietors' Association of New South Wales in providing the salary for a Research Assistant during part of the investigation; research facilities provided from the Commonwealth Research Grant to the University of Sydney; and valuable discussion with Professor C. E. Marshall in connection with the presentation of results.

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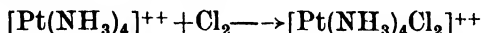
STUDIES IN THE CHEMISTRY OF PLATINUM COMPLEXES.

PART IV. OXIDATION OF IONS OF THE TETRAMMINE PLATINUM II TYPE WITH HYDROGEN PEROXIDE.

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Platinum (IV) compounds of the type $[\text{Pt}(\text{NH}_3)_4\text{Y}_2]\text{X}_2$ are, in general, prepared by oxidation of the tetrammine platinum (II) ion, using a source of the group it is desired to introduce as oxidising agent, when the compound of quadrivalent platinum is formed, e.g.,



When H_2O_2 is used as oxidising agent in aqueous solution the corresponding dihydroxo compound is formed.



Apart from salts of the dihydroxo tetrammine platinum (IV) ion, which are well known, compounds in which the ammonia groups are replaced by other coordinated groups do not appear to have been prepared previously.

In a previous communication it is reported that the attempted oxidation of tetra pyridine platinum II fluoride with hydrogen peroxide was unsuccessful. We have now made further attempts to oxidise the tetrapyridine platinum II ion with hydrogen peroxide. Reaction of the chloride of this ion with aqueous hydrogen peroxide under the same conditions used for oxidation of tetrammine platinum II chloride does not appear to bring about oxidation and tetrapyridine platinum (II) chloride can be recovered from the reaction mixture. An aqueous solution of the perchlorate does not discolour potassium permanganate.

Compounds in which one or more of the pyridine groups in the tetra pyridine platinum (II) ion are replaced by ammonia can be prepared.

Trans dipyridine diammine platinum (II) chloride reacts with hydrogen peroxide, oxidation taking place to yield the corresponding dihydroxo platinum IV chloride, from which other salts can be prepared by double decomposition in aqueous solution. These are generally colourless, crystalline compounds, moderately soluble in cold water and readily soluble in hot water. With potassium chloroplatinate (II) and chloroplatinic (IV) acid the ion yields sparingly soluble coloured compounds, the compound obtained from the chloroplatinate (II) being of uncertain structure, due to the possibility of simultaneous oxidation-reduction occurring. It has thus been shown that analogous reactions with hydrogen peroxide and the tetrammine platinum (II) ion occur when two of the ammonia groups are replaced by pyridine molecules. The $-\text{OH}$ groups are most likely in the trans or 1:6 positions.

In the postulate of essential electrical neutrality of atoms (Pauling, 1948) the charge on a complex ion is considered to be localised mainly on the peripheral hydrogen atoms of hexaquo or hexammine ions. If the postulate is extended to planar tetrammine ions of platinum (II) we can consider the greater portion of the charge of $2+$ located on the twelve hydrogen atoms in $[\text{Pt}(\text{NH}_3)_4]^{++}$

leaving the platinum atom with only fractional charge. With the tetrapyridine platinum (II) ion such a charge distribution is less favoured resulting in a numerically greater positive charge on the platinum atom. On the basis of this postulate it would appear that these structural differences are somehow intrinsically associated with the lack of reaction of the $[\text{PtPy}_4]^{++}$ with H_2O_2 . Replacement of two pyridine molecules by ammonia sufficiently alters the structure as to permit reaction with H_2O_2 .

The above example of the influence of attached pyridine groups on the reactions of a complex ion is probably one of a general type. Thus it has been shown (Friend and Mellor, 1947) that when trans-dichlorotetrapyridine cobalt (III) chloride reacts with pyridine, reduction occurs and tetrapyridine cobalt (II) chloride is formed, chlorine being liberated during the reaction. This suggests that a complex cobalt ion with more than four attached pyridine groups is incompatible with the increased charge required on the ion.

Evidence that, when the coordination number of a metal is satisfied by pyridine molecules, the lower oxidation state is favoured has been demonstrated by Dwyer and Nyholm (1942). These authors succeeded in preparing hexapyridine rhodium (II) compounds, halogeno pentapyridine rhodium (II) and other compounds in the pyridine rhodium (II) series. Attempts to prepare similar compounds of rhodium (II) containing ammonia and ethylenediamine were unsuccessful, only rhodium (III) compounds being obtained (private communication from Dr. F. P. J. Dwyer).

EXPERIMENTAL.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum IV Chloride 1.5 Hydrate.

Trans- $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Drew, Pinkard, Wardlaw and Cox, 1932) (1.0 g.) was treated with 30% H_2O_2 (6 ml.); oxygen was evolved and the temperature of the solution rose to about 35° C. On standing crystals were deposited in well formed cubes with some tetragonal forms present. Further crystallisation was induced by the addition of acetone. Yield 1.1 g. Recrystallised from hot water, yield 0.9 g., in small colourless tetragonal crystals of the 1.5 hydrate moderately soluble in water (about 6–7 g./100 g. at 5° C.). Over P_2O_5 the water of crystallisation was lost and regained on exposure to air.

Found (on air dry material): Pt, 37.6%; Cl, 13.8%.

H_2O , 4.8, 5.6. (Lost *in vacuo* over P_2O_5 .)

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{Cl}_2 \cdot 1.5 \text{H}_2\text{O}$ requires Pt, 37.6%; Cl, 13.7%; H_2O , 5.2%.

1 : 6 Dihydroxo-2 : 4 dipyridine diammine Platinum IV Bromide 2-Hydrate.

The corresponding chloride, recrystallised from water (1.0 g.) was dissolved in minimum quantity of hot water (5 ml.) and 0.7 g. of potassium bromide added. The clear solution was cooled in ice water, when the less soluble bromide crystallised. Yield 1.0 g. Recrystallised from hot water (7.5 ml.) as small colourless tetragonal crystals with (100) faces. The 2-hydrate obtained was only moderately soluble in cold water (about 2.8 g. per 100 g. water at 5–10° C.). Over P_2O_5 , 2 molecules of H_2O were lost but are taken up again on exposure to air.

Found (on air dry material): Pt, 31.7%; Br, 26.1%; H_2O , 5.6%. (Loss *in vacuo* over P_2O_5 .)

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ requires: Pt, 31.6%; Br, 25.9%; H_2O , 5.8%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Iodide 0.5 Hydrate.

Prepared from the corresponding chloride and potassium iodide in same manner as described for the bromide. 0.8 g. of the chloride yielded 0.7 g. of the iodide, recrystallised from water. The iodide was only sparingly soluble in water (about 0.5 g./100 g. H_2O at 5° C.), moderately soluble in hot water, from which it crystallised on cooling in colourless crystals of the 0.5 hydrate with tetragonal form showing (100) faces. The water of crystallisation was lost over P_2O_5 and regained on exposure to air.

Found (on air dry material) : Pt, 28.5% ; I, 37.1% ; H_2O , 1.2%. (Loss in *vacuo* over P_2O_5 .)

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{I}_2 \cdot 0.5\text{H}_2\text{O}$ requires : Pt, 28.5% ; I, 37.2% ; H_2O , 1.3%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Nitrate 1-Hydrate.

In an analogous manner to the preparation of the bromide and iodide, 1.0 g. of the chloride with ammonium nitrate yielded 0.6 g. of the nitrate 1-hydrate, recrystallised from water. It was sparingly soluble in water (about 3.8 g. in 100 g. at 5° C.), readily soluble in hot water, from which it crystallised in colourless tetragonal prisms. Water of crystallisation was lost on drying over P_2O_5 and regained on exposure to air. When heated the compound decrepitated.

Found (on air dry material) : Pt, 34.4% ; H_2O , 3.1%. (Loss in *vacuo* over P_2O_5 .)

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ requires : Pt, 34.6% ; H_2O , 3.2%.

1 : 6 Dihydroxo 2 : 4 dipyridine diammine Platinum (IV) Perchlorate.

As before from the corresponding chloride and perchloric acid, 1.0 g. of the chloride yielded 0.6 g. of the perchlorate recrystallised from hot water. The perchlorate was only moderately soluble in hot water and sparingly soluble in cold water (about 0.5 g./100 g. H_2O at 5° C.), from which it crystallised as colourless monoclinic needles and prisms. The anhydrous crystals were not deliquescent.

Found : Pt, 31.4%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2](\text{ClO}_4)_2$ requires : Pt, 31.4%.

Reaction of $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]^{++}$ with $(\text{PtCl}_4)^{--}$ and $[\text{PtCl}_6]^{--}$.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$ (0.49 g.) in a few ml. of water added to K_2PtCl_6 (0.4 g.) dissolved in the minimum quantity of water, gave an instantaneous precipitate which consisted of small thin, pink coloured plates, resembling graphite in form.

Yield : 0.6 g.

Found : Pt, 51.1%.

$\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2\text{PtCl}_4$ requires : Pt, 51.46%.

Similarly a solution of $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{Cl}_2$ in water with a solution of H_2PtCl_6 yielded an insoluble chloroplatinate (IV), in thin bright orange needles, sparingly soluble in hot water, moderately soluble in hot concentrated hydrochloric from which the chloride crystallises on cooling.

Found : Pt, 47.0%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2(\text{OH})_2]\text{PtCl}_6$ requires : Pt, 47.0%.

Trans-dipyridine diammine Platinum (II) Bromide 1-Hydrate.

Trans $[\text{Pt}(\text{C}_5\text{H}_5\text{N})_2(\text{NH}_3)_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Drew, Pinkard, Wardlaw and Cox, 1932) (0.7 g.) was dissolved in hot water (4 ml.) and 0.6 g. potassium bromide added. The bromide was precipitated immediately ; yield 0.7 g. Recrystallised from hot water (6 ml.) as colourless tetragonal needles and prisms. The hydrate obtained was only moderately soluble in cold water (2.7 g. per 100 g. water at 15° C.). Over P_2O_5 one molecule of H_2O is lost.

Found (on air dry material) : Pt, 34.5% ; Br, 28.6% ; H_2O , 2.94%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{Br}_2 \cdot \text{H}_2\text{O}$ requires : Pt, 34.5% ; Br, 28.3% ; H_2O , 3.18%.

Trans-dipyridine diammine Platinum II Iodide.

Prepared from the corresponding chloride and potassium iodide in the same manner as used for the bromide. 0.4 g. chloride yielded 0.33 g. of iodide, recrystallized from water. The iodide was sparingly soluble in water (0.5 g. per 100 g. of water at 15° C.), moderately soluble in hot water (about 4 g. per 100 g. water at 100° C.). It crystallized as anhydrous colourless tetragonal prisms.

Found : Pt, 30.4% ; I, 39.2%.

$[\text{Pt}(\text{C}_5\text{H}_5\text{N})_2(\text{NH}_3)_2]\text{I}_2$ requires : Pt, 30.4% ; I, 39.6%.

Trans-dipyridine diammine Platinum II Nitrate.

The nitrate was prepared from the chloride in a similar manner to the bromide and iodide. 0.6 g. of the chloride treated with ammonium nitrated yielded 0.6 g. of the nitrate, which on recrystallization from water yielded 0.22 g. The nitrate was only moderately soluble in cold water (about 6 g. per 100 g. water at 15° C.) but very soluble in hot water (about 40–50 g. per 100 g. at 100° C.), from which it crystallized in anhydrous colourless tetragonal needles and prisms.

Found : Pt, 38.3%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2](\text{NO}_3)_2$ requires : Pt, 38.2%.

Trans-dipyridine diammine Platinum II Perchlorate.

This was prepared by the addition of perchloric acid in a solution of the corresponding chloride. 0.8 g. of the chloride yielded 0.57 g. recrystallized from water. The perchlorate was only moderately soluble in hot water (about 6 g. per 100 g. water at 100° C.) and sparingly soluble (about 0.4 g. per 100 g. at 15° C.) in cold water, from which it crystallized as colourless monoclinic needles. The anhydrous crystals were not deliquescent.

Found : Pt, 33.1%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2](\text{ClO}_4)_2$ requires : Pt, 33.2%.

Trans-dipyridine diammine Platinum II Chloroplatinate (IV).

A solution of $[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2$ in water treated with a solution of H_2PtCl_6 yielded an insoluble chloroplatinate (IV). The product consisted of orange cubes, similar in shape to fluorite. It was found to be insoluble in cold water, very sparingly soluble in hot water, and moderately soluble in hot concentrated hydrochloric acid, from which the chloride crystallizes on cooling.

Found : Pt, 49.0%.

$[\text{Pt}(\text{NH}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{PtCl}_6$ requires : Pt, 49.0%.

SUMMARY.

The preparation of some compounds of the 1 : 6 dihydroxo 2 : 4 dipyridine diammine platinum (IV) ion has been described. The compounds were colourless crystalline compounds only moderately soluble in water. Coloured, insoluble, crystalline compounds were formed when the ion reacted with the chloroplatinate (II) and chloroplatinate (IV) ions. Attempted oxidation of the tetrapyridine platinum (II) ion with hydrogen peroxide, under similar conditions was unsuccessful.

ACKNOWLEDGEMENT.

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COORDINATION COMPOUNDS OF COPPER.

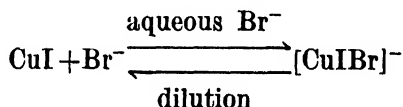
PART II. COMPOUNDS DERIVED FROM COPPER (I) IODIDE.

By C. M. HARRIS.

Manuscript received, July 31, 1950. Read, September 6, 1950.

Copper (I) halides readily dissolve in boiling concentrated solutions of the corresponding alkali or ammonium halides to form complex halogeno-cuprates (I). Recently the author employed this reaction (Harris, 1948) to isolate tetrammine and bis-ethylenediamine copper (II) dihalogeno-cuprates (I) of the general formula $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{X}_2]_2$ ($\text{A}=\text{NH}_3$; $2\text{A}=\text{C}_2\text{H}_4(\text{NH}_2)_2$ and $\text{X}=\text{Br}$ and I). With the chloro-complexes the ammonia compound was obtained as the monohydrate $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{Cl}_2]_2 \cdot \text{H}_2\text{O}$ and the ethylenediamine compound possessed the formula $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}_3\text{Cl}_5]$.

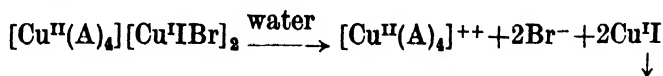
It has since been found that copper (I) iodide dissolves in a boiling concentrated solution of alkali or ammonium bromide forming a colourless solution presumably containing the bromo-iodo-cuprate (I) ion.



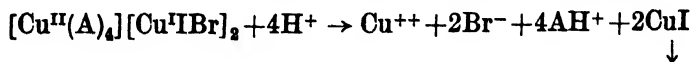
Dilution decomposes the complex ion causing copper (I) iodide to be precipitated. That this solution does contain such an ion and is not merely a mixture of the dibromo- and diiodo-cuprate (I) ions is supported by its reactions with ammonia and ethylenediamine described later.

Addition of a solution containing the bromo-iodo-cuprate (I) ion to a solution containing tetrammine copper (II) or bis-ethylenediamine copper (II) ions yields, on cooling, black tetrammine copper (II) bromo-iodo-cuprate (I) $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{IBr}]_2$ (I) and purple bis-ethylenediamine copper (II) bromo-iodo-cuprate (I) $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{IBr}]_2$ (II) respectively.

Water, particularly on heating, decomposes these compounds, forming a deep blue and



purple solution of tetrammine and bis-ethylenediamine copper (II) bromide respectively and a white precipitate of copper (I) iodide. Addition of acid decomposes the tetrammine ion as well according to the reaction



providing a means of determining the copper (II) ion in the presence of copper (I) since the addition of iodide ions liberates iodine equivalent to the copper (II).

Treatment of compound II with boiling concentrated potassium iodide solution causes it to dissolve and, on cooling, brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (Harris, *loc. cit.*) are deposited.

Compounds I and II cannot be a physical mixture of the corresponding dibromo- and diiodo-complexes since the diiodo-complexes liberate free iodine (Harris, *loc. cit.*) on treatment with acid and these compounds do not. However, the structures of compounds I and II in the solid state need not necessarily contain discrete $[\text{CuI}]\text{Br}^-$ ions. They could contain both $[\text{CuBr}_2]^-$ and $[\text{CuI}_2]^-$ ions.

The reaction of the bromo-iodo-cuprate (I) solution with a limited amount of ammonium hydroxide yielded, on cooling, an amminated copper (I) iodide derivative, $(\text{CuI})_2 \cdot \text{NH}_3$ (III), as white plates. On reacting a solution containing the diiodo-cuprate (I) ion in a similar manner with ammonium hydroxide an entirely different compound, $\text{CuI} \cdot \text{NH}_3$ (IV), was obtained as yellow prisms. This reaction supports the postulation of the bromo-iodo-cuprate (I) ion in solution indicating that such a solution is not merely a mixture of $[\text{CuI}_2]^-$ and $[\text{CuBr}_2]^-$ ions since if this was the case it should yield the same copper (I) iodide derivative with ammonia as a solution containing only $[\text{CuI}_2]^-$ ions.

Ethylenediamine fails to react with the bromo-iodo-cuprate (I) solution to yield a copper (I) iodide derivative. On shaking the mixture in the presence of air, oxidation takes place and purple prisms of compound II are deposited. The diiodo-cuprate (I) solution reacts immediately with ethylenediamine to deposit a cream microcrystalline compound, $(\text{CuI})_2 \cdot \text{C}_2\text{H}_4(\text{NH}_2)_2$ (V). The filtrate deposited brown prisms of a compound which was most likely bis-ethylenediamine copper (II) diiodo-cuprate (I) resulting from oxidation of copper (I).

The structure of compound III is unknown. Silberrad (1905) reported the preparation of a green compound $\text{Cu}_2\text{I}_2 \cdot \text{NH}_3 \cdot 4\text{H}_2\text{O}$. Since the preparation was performed in the presence of air in a strongly ammoniacal solution and the water was determined by difference it is quite possible that this compound was an oxidised copper (I) derivative in keeping with its colour.

Compound IV can be formulated as either the monomer $[\text{H}_3\text{N} \rightarrow \text{CuI}]^\circ$, the dimer $[\text{Cu}^\text{I}(\text{NH}_3)_2][\text{Cu}^\text{I}\text{I}_2]$, or the tetramer $[\text{H}_3\text{N} \rightarrow \text{CuI}]_4^\circ$. The last structure is similar to the triethyl arsine derivative $[\text{Et}_3\text{As} \rightarrow \text{CuI}]_4^\circ$, whose structure was established by Mann, Purdie and Wells (1936) to consist of a central tetrahedron of copper atoms surrounded by tetrahedral groups of iodine atoms and triethyl arsine molecules. This structure would seem the most likely.

A number of alternative structures are possible for compound V also. It may be formulated as the complex copper (I) cuprate (I), $[\text{Cu}^\text{I}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^\text{I}\text{I}_2]$. This, however, seems unlikely, since apart from a lack of symmetry the $[\text{Cu}^\text{I}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2]^+$ ion would involve considerable strain in the carbon-nitrogen bonds if it was to possess the linear configuration which is associated with two covalent copper (I) complexes (Wells, 1945). This view is supported by the fact that no compounds containing the ethylenediamine copper (I) ion are known. Compound V can be satisfactorily formulated with a tetrahedral structure similar to the arsine derivative mentioned previously save that the intramolecular bridging that would be required of ethylenediamine for the existence of discrete tetrahedral molecules in the structure is unlikely from a consideration of bond lengths and angles. An infinite three-dimensional structure, however, would be possible with intermolecular bridging of the tetrahedral units by means of the ethylenediamine.

Compounds corresponding to III and IV have previously been postulated by Biltz and Stollenwerk (1921). They investigated tensimetrically the formation of ammoniates with copper (I) halides and in the case of the iodide obtained evidence for the existence of the ammoniates $\text{CuI} \cdot n\text{NH}_3$ where $n=0.5, 1, 2$ and 3.

During the course of this work an attempt was made to form the diammine (ethylenediamine) copper (II) ion, $[\text{Cu}(\text{NH}_3)_2(\text{C}_2\text{H}_4(\text{NH}_2)_2)]^{++}$, in solution and isolate it as its diiodo-cuprate (I) derivative. This was not realised and on reacting one mole of a copper (II) salt with one mole of ethylenediamine and a limited excess of ammonium hydroxide followed by metathesis with a potassium iodo-cuprate (I) solution an earth green mixture of tetrammine and bis-ethylene-diamine copper (II) diiodo-cuprates (I) was obtained. The tetrammine compound in the mixture was decomposed to copper (I) iodide by heating the mixture at 100°C . to constant weight. From the loss in weight was calculated the percentage of tetrammine compound present. The residue was treated with concentrated potassium iodide solution to remove copper (I) iodide and the bis-ethylenediamine compound that remained was filtered off and identified.

Compounds I-V inclusive reduce silver nitrate solution to the metal instantly in the cold due to the copper (I) present in their molecules and also give a simultaneous precipitate of silver halide. They are insoluble in the usual organic solvents and unstable to water.

Copper (I) iodide also dissolves to a small extent in boiling concentrated ammonium and alkali chloride solutions presumably forming the chloro-iodo-cuprate (I) ion. Attempts to isolate this ion as its bis-ethylenediamine copper (II) derivative were unsuccessful due to the large amounts of ammonium or alkali chloride that crystallised out on cooling the reaction mixture.

EXPERIMENTAL.

(I) Tetrammine Copper (II) Bromo-iodo-cuprate (I).

To diammine copper (II) acetate (1.6 g., 0.0074 g. mole (Horn, 1908)) dissolved in a solution of ammonium hydroxide (1.3 ml. of 15 N) in water (25 ml.) was added acetic acid (0.3 ml. of 17 N). After the addition of ammonium bromide (5.0 g.) the solution was heated to $80-85^\circ\text{C}$. A boiling solution of copper (I) iodide (2.8 g., 0.015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added in a thin stream with constant stirring and the stirring continued while the solution was cooled to 25°C . After immediate filtration the black microcrystals were washed with 90% alcohol, followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. Yield 2.4 g. (42%).

Found: Cu (total), 28.2; Cu^{++} , 9.31; NH_3 , 10.1%. 0.497 and 0.502 g. complex gave 0.623 and 0.631 g. of $\text{AgBr} + \text{AgI}$.

$[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{IBr}]_2$ requires Cu (total), 28.36; Cu^{++} , 9.45; NH_3 , 10.13%. 0.497 and 0.502 g. complex give 0.625 and 0.631 g. of $\text{AgBr} + \text{AgI}$.

The compound is readily oxidised in the presence of moist air, assuming a greenish colour. Water decomposes it instantly in the cold, according to the reaction given previously. It is unaffected by alcohol, acetone and the usual organic solvents. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver with simultaneous precipitation of silver halides.

(II) Bis-ethylenediamine Copper (II) Bromo-iodo-cuprate (I).

To a solution of bis-ethylene diamine copper (II) bromide monohydrate (2.5 g., 0.0069 g. mole (Johnson and Bryant, 1934)) dissolved in water (30 ml.) was added ammonium bromide (5.0 g.), and the solution was heated to 85°C . A boiling solution of copper (I) iodide (2.6 g., 0.015 g. mole) and ammonium bromide (30 g.) in water (35 ml.) was added with constant stirring and the stirring continued while the solution was cooled to 25°C . After filtration the compound was washed with methyl alcohol followed by dry ether. Yield 4.6 g. (92%).

Found: Cu (total), 26.4; Cu^{++} , 8.73%. 0.496 g. complex gave 0.474 g. $\text{AgBr} + \text{AgI}$.

$[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{IBr}]_2$ requires Cu (total), 26.3; Cu^{++} , 8.77%. 0.496 g. complex gives 0.479 g. $\text{AgBr} + \text{AgI}$.

The compound crystallises as purple prisms stable in air. Water decomposes the compound more slowly than the corresponding tetrammine but completely on boiling in accordance with the equation given previously. It reduces silver nitrate solution instantly in the cold to silver with simultaneous precipitation of silver halides. Dilute acetic and sulphuric acid decomposes the compound, according to the equation given previously to copper (I) iodide. (Found: Cu, 66.0; calculated: Cu, 66.6%.) The compound dissolves in boiling 50% potassium iodide solution, from which brown prisms of bis-ethylenediamine copper (II) diiodo-cuprate (I) (*loc. cit.*) is deposited on cooling. (Found: Cu (total), 23.4; calculated: Cu (total), 23.3%.) The compound is unaffected by alcohol, acetone and the usual organic solvents.

(III) *Monammine Bis-(Copper (I) Iodide).*

To copper (I) iodide (2.0 g.) dissolved in a boiling solution of potassium bromide (35 g.) in water (50 ml.) and cooled to 85° C. was added ammonium hydroxide (0.70 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with 90% alcohol followed by dry ether. The filtration and washing must be as rapid as possible to avoid oxidation. The ether was removed under vacuum and the compound sealed from the atmosphere. Yield 0.8 g. (38%).

Found: Cu, 31.4; NH_3 , 4.4; I, 63.8%. $(\text{Cu}^{\text{I}}\text{I})_2\text{NH}_3$ requires Cu, 31.9; NH_3 , 4.3; I, 63.8%.

The compound crystallises as lustrous pearly plates and is readily oxidised in the atmosphere assuming a green colour. It is decomposed immediately in the cold by water, with the appearance of the blue tetrammine copper (II) colour due to oxidation. A cold solution of silver nitrate is instantly reduced by the compound to metallic silver, with simultaneous precipitation of silver iodide. On heating at 100° C. to constant weight the compound (0.202 g.) loses its ammonia, and copper (I) iodide (0.192 g.) (calc. 0.193 g.) remains. It is insoluble in organic solvents.

(IV) *Monammine Copper (I) Iodide.*

To copper (I) iodide (7.5 g.) dissolved in a boiling solution of potassium iodide (45 g.) in water (30 ml.) and cooled to 75° C. was added ammonium hydroxide (2.5 ml. of 15 N) with vigorous stirring. The stirring was continued while the solution was rapidly cooled to 25° C. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. The ether was removed and the compound sealed from the atmosphere. Yield 5.0 g. (61%).

Found: Cu, 30.3; NH_3 , 8.2; I, 61.3%.

$\text{Cu}^{\text{I}}\text{I}\cdot\text{NH}_3$ requires Cu, 30.6; NH_3 , 8.2; I, 61.2%.

The compound is decomposed by water similarly to the previous compound and gives the same reaction with silver nitrate. It crystallises as yellow prisms, readily oxidised by the atmosphere, when it assumes a green colour.

(V) *Ethylenediamine Bis-(Copper(I) Iodide).*

To copper (I) iodide (2.9 g., 0.015 g. mole) dissolved in a boiling solution of potassium iodide (22 g.) in water (15 ml.) and cooled to 55° C. was added a solution of ethylenediamine (0.40 ml. of anhydrous, 0.006 g. mole) and potassium iodide (5.0 g.) in water (5 ml.) at 55° C. with stirring. After immediate filtration the compound was washed with methyl alcohol followed by dry ether. Yield 2.6 g. (98%).

Found: Cu, 28.7; I, 57.6%.

$(\text{Cu}^{\text{I}}\text{I})_2\cdot\text{C}_2\text{H}_4(\text{NH}_2)_2$ requires Cu, 28.8; I, 57.5%.

The compound is insoluble in organic solvents and is stable in air. It crystallises as cream micro-prisms and reduces silver nitrate in the cold to metallic silver with simultaneous precipitation of silver iodide. It is insoluble in cold water but decomposed readily on warming, oxidation to bis-ethylenediamine copper (II) iodide taking place (see Morgan and Burstal, 1926). The filtrate from the above preparation deposited a small amount of brown prisms which were probably bis-ethylenediamine copper (II) diiodo-cuprate (I), resulting from partial oxidation of some of the copper (I).

Reaction of Ethylenediamine with a Solution of the Bromo-iodo-cuprate (I) Ion.

To copper (I) iodide (1.0 g.) dissolved in a boiling solution of ammonium bromide (20 g.) in water (20 ml.) and cooled to 60° C. was added a solution of ethylenediamine (0.15 ml. of anhydrous) in water (5 ml.) containing ammonium bromide (5.0 g.) at 55° C. No precipitate appeared on cooling to 30° C. but on shaking for 10–15 minutes purple prisms of compound II were deposited. Yield 0.5 g.

Found: Cu (total), 26.4.

Calculated: 26.3%.

Attempted Preparation of Diammine (Ethylenediamine) Copper (II) Diiodo-cuprate (I).

To a solution of anhydrous copper (II) chloride (0.85 g., 0.0063 g. mole) in water (15 ml.) was added ethylenediamine (0.62 ml. of 69%, 0.0071 g. mole) followed by ammonium hydroxide (1.0 ml. of 15N). After the addition of potassium iodide (2.0 g.) the stirred solution was heated to 75° C. and to it was added in a fine stream a boiling solution of copper (I) iodide (2.4 g., 0.013 g. mole) and potassium iodide (15.0 g.) in water (10 ml.). The stirring was continued and the solution cooled to 25° C. After filtration the compound was washed with 90% alcohol followed by ether. Yield 4.4 g.

Found: Cu, 23.8%.

Calculated for a 1:2 mixture of $[\text{Cu}^{\text{II}}(\text{NH}_3)_4][\text{Cu}^{\text{I}}\text{I}_2]_2$ and $[\text{Cu}^{\text{II}}(\text{C}_2\text{H}_4(\text{NH}_2)_2)_2][\text{Cu}^{\text{I}}\text{I}_2]_2$: Cu, 23.8%.

The mixture, which was micro-crystalline, possessed an earthy colour with a green reflex. Brown and dark green crystals could be distinguished under the microscope. The mixture (0.511 g.) was heated to 100° C. to constant weight (0.468 g.). From the loss in weight (0.043 g.) the amount of tetrammine copper (II) diiodo cuprate (I) (0.173 g.) present in the mixture was calculated.

The residue was boiled with 50% potassium iodide solution (10 ml.) and on cooling to 30–40° C. the brown bis-ethylenediamine copper (II) diiodo-cuprate (I) was filtered off and washed with 50% potassium iodide solution (5 ml.) followed by methyl alcohol and ether. Yield 0.29 g.

Found: Cu, 23.3%.

Calculated: 23.3%.

SUMMARY.

Copper (I) iodide dissolves in concentrated ammonium or alkali bromide solution to form the bromo-iodo-cuprate (I) ion. Double decomposition of solutions containing this ion with solutions of tetrammine and bis-ethylenediamine copper (II) ions yields the corresponding tetrammine and bis-ethylenediamine copper (II) bromo-iodo-cuprates (I) of general formula $[\text{Cu}^{\text{II}}(\text{A})_4][\text{Cu}^{\text{I}}\text{IBr}]_2$. Solutions containing the bromo-iodo-cuprate (I) ion give with ammonium hydroxide a compound of empirical formula $(\text{CuI})_2\cdot\text{NH}_3$, whose structure is unknown. With ethylenediamine, however, partial oxidation takes place and bis-ethylenediamine copper (II) bromo-iodo-cuprate (I) is obtained. Similarly solutions of the diiodo cuprate (I) ion yields with ammonia and ethylenediamine compounds of empirical formula $\text{CuI}\cdot\text{NH}_3$ and $(\text{CuI})_2\cdot\text{C}_2\text{H}_4(\text{NH}_2)_2$ respectively. Possible structures for these compounds are suggested. Attempts to prepare diamine (ethylenediamine) copper (II) diiodo-cuprate (I) were unsuccessful.

ACKNOWLEDGEMENTS.

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THE CHEMISTRY OF OSMIUM.

PART VII. THE BROMO AND CHLORO PENTAMMINE OSMIUM III SERIES.

By F. P. DWYER, D.Sc.,
and J. W. HOGARTH, A.S.T.C.

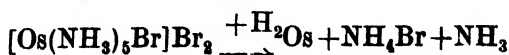
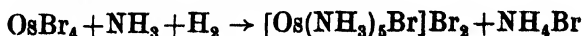
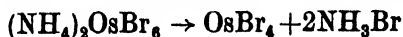
Manuscript received, September 13, 1950. Read, October 4, 1950.

With the exception of the osmyl amines $\text{OsO}_2(\text{NH}_3)_4\text{X}_2$ (W. Gibbs, 1881), no complex compounds of osmium containing ammonia, pyridine or ethylenediamine are known.

The curious substance potassium osmiate $\text{K}(\text{OsO}_3\text{N})$, a compound of octavalent osmium has been prepared by treatment of osmium tetroxide with ammonia and aqueous potassium hydroxide (Fritsche and Struve, 1847; L. Brizard, 1900). It reacts with hydrochloric acid with the liberation of chlorine and degradation to the hexavalent state to form $\text{K}_2(\text{OsCl}_5\text{N})$, which is reducible with stannous chloride to potassium amino pentachloro osmate IV $\text{K}_2(\text{Os}(\text{NH}_2\text{Cl}_5))$ (Werner and Dinklage, 1901).

Attempts to prepare osmium amines by reaction of potassium hexachloro or hexabromo osmate IV with aqueous ammonia led to hydrolysis, with the separation, ultimately, of a black precipitate of (presumably) osmium dioxide. Similarly, solutions of potassium hexachloro or hexabromo osmate III (Dwyer, McKenzie and Nyholm, 1945; Dwyer, Humpoletz and Nyholm, 1946) darkened in colour and also, ultimately, a black precipitate resulted. The molecules of arsine in tris-dimethylphenyl arsine tri-bromo-osmium could not be replaced by boiling the compound with alcoholic ammonia. Instead, partial replacement of the bromine atoms by hydroxyl occurred (unpublished observations of Barclay and Dwyer, 1948). By analogy with platinum, palladium, ruthenium and iridium it appeared probable that direct ammination could not be achieved in the tetravalent state, and consequently the osmium must be reduced to the strongly reducing trivalent or bivalent states and then treated with ammonia in the absence of both oxygen and water. It was thought possible that these conditions could be realised simultaneously by heating a tetravalent osmium compound in dry ammonia gas. If necessary, preheating of the gas could be arranged to provide various pressures of hydrogen by thermal dissociation of the ammonia. The initial experiments with potassium hexachloro or hexabromosmate IV were not successful, either no reaction occurring or complete reduction to osmium metal. However, with ammonium hexabromosmate IV, a sublimate of ammonium bromide was observed to form at 260° . When ammonia gas was passed over the compound in a small porcelain boat at 280° a further sublimate appeared with change of colour of the complex salt from dark red to brownish, and at 300° more ammonium bromide appeared and a silvery deposit of osmium remained.

The following changes appeared to occur :



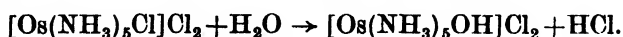
The yields of the osmium ammine, however, were poor and the reaction difficult to control. The initial experiments carried out in an autoclave with one or two atmospheres pressure of ammonia were not successful. Eventually it was found necessary to subject the ammonium bromosmate to 7 or 8 atmospheres pressure for a short time and then reduce the pressure to 2 atmospheres. When then heated at 285° for $1\frac{1}{2}$ to 2 hours a quantitative conversion to almost white bromo pentammine osmium III bromide was found to have occurred. Although much of the gas must have been consumed in the reaction, at the end, the ammonia pressure was found to have barely altered. When the initial high pressure was applied to the ammonium bromosmate it was found to have dissolved to a red solution in liquid ammonia. With subsequent lowering of the pressure the liquid boiled away but must have left a loose addition compound $(\text{NH}_4)_2\text{OsBr}_6 \cdot x\text{NH}_3$, which is apparently transformed to the ammine. This will be investigated further. Bromopentammine osmium III bromide $(\text{Os}(\text{NH}_3)_5\text{Br})_2\text{Br}_2$, obtained as a light fawn coloured micro-crystalline powder by precipitation of the aqueous solution, had powerful reducing properties, reacting with silver nitrate to form a precipitate of the silver halide, and on warming reducing the excess to metallic silver. With bromine water, oxidation and precipitation of an orange osmium IV ammine resulted. These compounds will be discussed in subsequent papers.

The iodide, $[\text{Os}(\text{NH}_3)_5\text{Br}]\text{I}_2$, the nitrate $[\text{Os}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$, and the perchlorate $[\text{Os}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2$ were obtained as light brown or fawn micro-crystalline powders by double decomposition. The reaction with silver chloride gave a mixture of the hydroxy pentammine chloride, $[\text{Os}(\text{NH}_3)_5\text{OH}]\text{Cl}_2$, and the bromopentammine chloride, $[\text{Os}(\text{NH}_3)_5\text{Br}]\text{Cl}_2$. The former compound was transformed to chloropentammine osmium III chloride by treatment with hydrochloric acid.

Morgan and Burstall (1936) noted a similar case of transformation of chloro-hydroxy-tetrammine ruthenium III chloride to dichlorotetrammine ruthenium III chloride.

Under 7-8 atmospheres pressure of ammonia gas, bromo-pentammine osmium III bromide was found to dissolve to a greenish solution. Evaporation of the liquid ammonia left a green substance, which appeared to be a mixture of the original compound and the hexammine $[\text{Os}(\text{NH}_3)_6]\text{Br}_3$. The reaction is being investigated.

Chloro pentammine osmium III chloride was obtained from ammonium chlorosmate in the same way as the bromo compound. The almost white microcrystalline powder had an acid reaction to litmus and partly replaced the covalent halogen atom by hydroxyl on heating the aqueous solution.

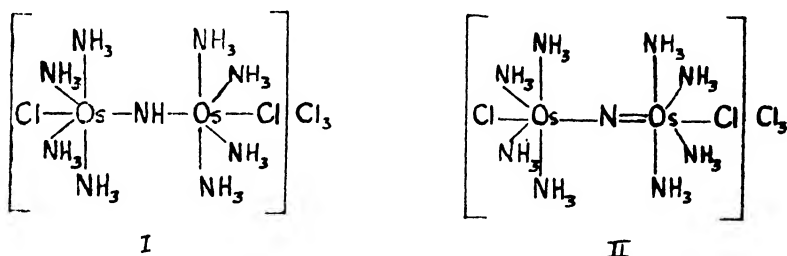


The lability of the chlorine atom, due to its ionic character, made the preparation of derivatives such as $(\text{Os}(\text{NH}_3)_5\text{Cl})\text{I}_2$ impossible. The chloro compound was also more sensitive to atmospheric oxidation than the bromo compound. Specimens of the solid after 10-14 days exposure to the atmosphere had little reducing action on silver nitrate, and appeared to be almost completely transformed to $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot \text{OH}$.

During the preparation of the chloro pentammine compound, it was found that, provided small samples of 0.1-0.3 g. of ammonium hexachlorosmate were used, complete transformation to the white pentammine occurred—but with larger amounts of the hexachlorosmate (0.5-1.0 g.) a mixture of white and yellow powders was obtained. The top crust and the edges of the reaction product were usually white, whilst the centre was brownish yellow. The yellow product was insoluble in 0.5 N hydrochloric acid but soluble in water. From

the brownish aqueous solution it was precipitated easily with hydrochloric acid and separated from the chloropentammine compound.

The formula of the anhydrous compound was found to be $\text{Os}_2(\text{NH}_3)_8\text{NHCl}_5$, I, or $\text{Os}(\text{NH}_3)_5\text{NCl}_5$, II. Three of the chlorine atoms were ionised, and on treatment with cold sodium iodide, the substance $[\text{Os}_2(\text{NH}_3)_8\text{NHCl}_2]\text{I}_3$ or $[\text{Os}(\text{NH}_3)_5\text{NCl}_2]\text{I}_3$ was obtained. The yellow substance had no reducing action on aqueous silver nitrate and thus presumably was a compound of Osmium IV. On heating in the autoclave with ammonia gas at 300°C ., it was partially transformed to chloropentammine osmium III chloride.



In the structural formula I, one Os atom is formally trivalent and the other quadrivalent. However, both atoms would probably have the same valence by reason of a resonance phenomenon. This should lead to an intense colour. The pale colour, especially of the solutions, is a possible objection to I. In the structure II both atoms are quadrivalent, and this formula is to be preferred by analogy with the nitrilo complexes $\text{K}_2[\text{OsN}.\text{Cl}_5]$. Owing to the difficulty of carrying out hydrogen analyses in the presence of osmium, it is not possible to distinguish analytically between I and II. The substance in aqueous solution reacted acid, with darkening of colour on standing, due probably to replacement of the covalent Cl atoms by hydroxyl.

Titration with silver nitrate potentiometrically also confirmed that three chlorine atoms were ionised. The titration value, however, was a little high, indicating that some of the covalent chlorine atoms were replaced. The conductivity assuming formula II, for $1 \times 10^{-3}\text{M}$ and $2 \times 10^{-4}\text{M}$ solutions was found to be 499 mhos.

EXPERIMENTAL.

Bromopentammine Osmium III Bromide Monohydrate.

Ammonium bromosmate IV in two small platinum boats was suspended in the centre of a still autoclave fitted with a steel needle valve, and pressure gauge. A steel tube led through the head of the autoclave to near the bottom so that the ammonia gas could be used to sweep out the air. The air was displaced at approximately 0.5 at. of NH_3 gas by allowing the head of the autoclave to lift, then the head was screwed down and the full pressure of an ammonia cylinder (90–115 lb./sq. in.) applied for 20–30 mins. With excessive time of exposure to high pressure the boats tended to fill with liquid ammonia and overflow. The pressure was then reduced to 2 atmospheres and the autoclave heated in an oil bath with the external temperature adjusted to give 285°C . at the platinum boats. After $1\frac{1}{2}$ –2 hours the autoclave was removed from the oil bath and allowed to cool. The white powder left in the boats was ground up finely and extracted with warm dilute hydrobromic acid (approx. 0.1 N). The pale yellow solution was filtered from a small amount of dark substance, and ammonium bromide added. The pentammine precipitated as a pale fawn powder, and the precipitation was completed by cooling in ice. After washing with 90% alcohol the substance was dried over calcium chloride. On heating, the compound darkened considerably, leaving ultimately a deposit of osmium. It was insoluble in alcohol and acetone, but easily soluble in warm water. The density was found to be 2.49. The

equivalent conductivities of 1×10^{-3} and 2×10^{-4} M solutions were found to be 248 and 229 mhos., showing the compound to be a ternary electrolyte. On treatment with a slight excess of silver nitrate, followed by potentiometric titration with potassium chloride, almost all of the bromine appeared to have precipitated.

Found : Br = 42.1%.

Calculated : Br = 30.02%. Total Br = 45.03%.

The osmium analyses were carried out in a micro porcelain boat by heating 2-8 mg. of the substance in oxygen-free ammonia gas up to a temperature of 460° C., and then weighing the osmium metal. This procedure was not suitable for the perchlorate or nitrate for which a colorimetric method (Dwyer and Gibson, 1950) was used.

Found : Os = 35.6 ; N = 13.0 ; Br = 44.93%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$: Os = 35.68 ; N = 13.11 ; Br = 45.03%.

Bromopentammine Osmium III Iodide.

The bromopentammine bromide, in warm water, was treated with a little potassium iodide. The substance crystallised as sparingly soluble dark yellow micro prisms on scratching the sides of the vessel. The compound was washed with alcohol and dried at 100° C.

Found : Os = 31.1%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}]\text{I}_2$: Os = 31.23%.

Bromopentammine Osmium III Nitrate.

The bromopentammine bromide in warm water was treated with solid ammonium nitrate when the sparingly soluble nitrate of the complex crystallised in brownish yellow prisms. It was washed with 80% alcohol and dried at 100°. The substance decomposed at approximately 200° C. with a slight explosion and a black cloud of osmium metal.

Found : Os = 39.3%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}](\text{NO}_3)_2$: Os = 39.7%.

Bromopentammine Osmium III Perchlorate Monohydrate.

This substance from sodium perchlorate and the bromopentammine bromide gave a brownish yellow sparingly soluble micro-crystalline powder. It exploded on heating.

Found : Os = 33.27%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$: Os = 33.24%.

Bromopentammine Osmium III Hexabromosmate IV Dihydrate.

A solution of potassium hexabromosmate IV in dilute hydrobromic acid was added to an aqueous solution of the bromopentammine bromide. The dark reddish brown microcrystalline precipitate was washed with alcohol and dried at 100° C.

Found : Os = 35.62%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}](\text{OsBr}_6) \cdot 2\text{H}_2\text{O}$: Os = 35.86%.

Bromopentammine Osmium III Hexachloroplatinate IV.

A solution of chloroplatinic acid was added to an aqueous solution of the bromopentammine bromide. The resulting orange yellow precipitate was washed with alcohol.

Found : Os + Pt = 46.15%.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Br}][\text{PtCl}_6] \cdot 2\text{H}_2\text{O}$: 46.7%.

The Action of Silver Chloride in Bromopentammine Osmium III Bromide.

A saturated solution of the bromopentammine bromide at 35° C. was shaken with silver chloride for 5 minutes and then filtered. The pale yellow filtrate was precipitated with alcohol to yield a white colloidal suspension which was coagulated with concentrated hydrochloric acid. (This also served to hold traces of silver chloride in solution as the acid $\text{H}.\text{AgCl}_4$. Otherwise these traces were precipitated as, presumably, the pentammine osmium salt of the acid.) The

pale fawn substance was washed with 90% alcohol and dried at 100° C. It was very soluble in water and reduced silver nitrate to the metal on boiling. Found: Os=46.2%. The bromopentammine osmium chloride requires Os=44.6%. Another specimen prepared by longer shaking with silver chloride and allowed to stand overnight in the alcohol hydrochloric acid mixture gave Os=48.1. The chloropentammine osmium III chloride hemihydrate requires Os=48.68%. Tests on this sample for bromine gave negative results. It was not possible to isolate the initial compound formed in the reaction between silver chloride and the bromopentammine bromide, since it could not be induced to coagulate without adding some contaminating ion. Specimens allowed to coagulate by long standing had undergone oxidation since they no longer reduced silver nitrate.

Chloropentammine Osmium III Chloride Hemihydrate.

Ammonium hexachlorosmate IV was heated in small platinum boats in ammonia gas as for the bromo compound (*vide supra*), except that the temperature was raised to 290–295°. At the end of the reaction the product consisted of a mixture of almost white material with a yellowish incrustation. With small quantities of ammonium hexachlorosmate (0.1–0.2 g.) the yellow material was almost absent. The mixture was ground up finely in a mortar and extracted three times with small amounts (10–15 c.c.) of 0.5 N HCl and filtered. The dark coloured precipitate was reserved (see later) and the pale yellow filtrate precipitated by the addition of alcohol. The resulting very pale fawn coloured powder was washed with alcohol, redissolved in the minimum of 0.5 N hydrochloric acid and traces of a yellow compound filtered off. It was then reprecipitated with alcohol and dried at 100° C. The substance was much more soluble in water than the bromo compound, the solution was acid (pH 4.5) due to partial replacement of the covalent halogen by hydroxyl. On reprecipitation from water with alcohol: found Cl=19.95%; Os=53.18%. Calculated for $[\text{Os}(\text{NH}_3)_5\text{OH}]\text{Cl}_2$: Cl=19.54; Os=54.9%.

The chloropentammine chloride reduced warm silver nitrate to the metal rapidly but specimens of the solid after two or three weeks failed in this reaction and hence must have undergone oxidation.

Found: Os=49.6, 49.04, 48.8, 48.6, 48.5, 48.8 (on different preparations); N=18.11; Cl=27.0.

Calculated for $[\text{Os}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$: Os=48.67; Cl=27.25; N=17.91%.

Dichloro-octammine-μ-nitrilo-diosmium Trichloride.

The residue from the extraction of the chloropentammine osmium III chloride with 0.5 N hydrochloric acid was extracted with water at 40° C. The resulting brownish orange solution was treated with hydrochloric acid, when it lost its brown colour becoming orange yellow and depositing a brownish yellow crystalline precipitate. This was filtered, washed with hydrochloric acid and alcohol and dried at 100°. The substance was found to be easily soluble in cold water, becoming brownish on heating. The solution, which had an acid reaction, precipitated the solid on the addition of hydrochloric acid or chloride ion. It gave a precipitate of silver halide on treatment with silver nitrate, but caused no reduction to the metal on boiling.

On standing over P_2O_5 or heating at 130° C., two molecules of water were lost without visible change in colour or form.

Found, undried substance: Os=50.5; N=16.9; Cl=23.78%; H_2O =4.2%.

Calculated for $\text{Os}_2(\text{NH}_3)_8\text{N} \cdot \text{Cl}_3 \cdot 2\text{H}_2\text{O}$: Os=51.1%; N=16.93; Cl=23.85; H_2O =4.8.

Found, anhydrous substance: Os=53.1; N=17.5; Cl=25.05; Cl (ionised)=16.8%.

Calculated for $\text{Os}_2(\text{NH}_3)_8\text{N} \cdot \text{Cl}_3$: Os=53.7; N=17.79; Cl=25.07; Cl (ionised)=15.04.

Dichloro-octammine-μ-nitrilo-diosmium Tri-iodide.

The chloro compound above, in water, was treated with a few drops of hydrochloric acid to suppress hydrolysis and sodium iodide added. The resulting yellow brown precipitate was filtered off immediately, washed with alcohol and dried at 100°.

Found: Os=38.6; N=12.9%.

Calculated for $[\text{Os}_2(\text{NH}_3)_8\text{N} \cdot \text{Cl}_2]\text{I}_3$: Os=38.8; N=12.81.

Di-iodo-Octammine-μ-diosmium Trichloride.

The chloro compound in hot water containing hydrochloric acid was heated at 80° with excess sodium iodide and cooled. The brownish yellow microcrystalline precipitate was washed with hydrochloric acid and alcohol.

Found: Os=43.4; N=14.17%.

Calculated for $[\text{Os}_2(\text{NH}_3)_8\text{NI}_2]\text{Cl}_3$: Os=42.60; N=14.12%.

SUMMARY.

Ammonium hexabromo and hexachlorosmate IV reacted with ammonia gas under pressure at 280–300° C. with the formation of bromopentammine osmium III bromide, and chloropentammine osmium III chloride. These compounds were pale fawn solids soluble in water to pale yellow solutions, which reduced silver nitrate solution to the metal on boiling. The covalently attached halogens were labile, especially in the chloro compound, whose aqueous solution had an acid reaction due to the replacement of chlorine by hydroxyl.

The curious compound $\text{Os}_2(\text{NH}_3)_8\text{NCl}_5 \cdot 2\text{H}_2\text{O}$ formulated dichloro-octammine-μ-nitrilo-diosmium trichloride was formed during the reaction of ammonium hexachlorosmate with ammonia.

ACKNOWLEDGEMENTS.

The authors are indebted to Miss E. C. Gyarfas and Mr. N. A. Gibson for assistance with some of the analyses; to Richard Wildridge Pty. Ltd. for the loan of the ammonia pressure gauge; and to Messrs. Patterson and Spooner for some of the apparatus.

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THE CHEMISTRY OF IRIIDIUM.

PART V. THE OXIDATION OF IRIIDIUM III SALT SOLUTIONS.

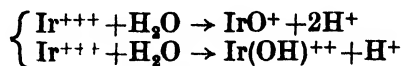
By F. P. DWYER, D.Sc.,
and (MISS) E. C. GYARFAS, M.Sc.

Manuscript received, September 15, 1950. Read, October 4, 1950.

This study has been undertaken as a preliminary to the investigation of the fluorides of iridium, in which the bond Ir-F may be expected to be predominantly ionic. The nitrates, perchlorates and, to a lesser extent, the sulphates, can be expected to be ionic and hence likely to give useful information concerning the fluorides.

Little is known of the simple salts of tetravalent iridium such as the nitrate, sulphate and perchlorate, attention having been confined almost exclusively to the covalent chloride and bromide, and to various complex compounds, of which the hexahalogenates R_2IrCl_6 are the best defined. It has been noted very long ago (Le de Boisbaudron, 1883 ; Marino, 1904) that the yellow solutions of iridium III sulphate, $\text{Ir}_2(\text{SO}_4)_3$, became green or blue on standing in air, and the colour change has been ascribed to the existence of varying amounts of salts in higher oxidation states. Similarly, the nitrate, prepared by dissolution of iridium III hydroxide in dilute nitric acid, can be obtained as a yellow solution, which rapidly becomes blue on standing or warming. Although the substance responsible for the blue colour has not been isolated it has been generally inferred that a higher oxidation state than trivalent iridium is present.

In the present work solutions of iridium III hydroxide in sulphuric, perchloric and nitric acids have been potentiometrically titrated with a variety of oxidising agents, or oxidised anodically and potentiometrically reduced. All of the iridium III salt solutions were oxidisable by bromine water with the development of a blue colour, discharged by the addition of ferrous sulphate. After such oxidation and reduction, however, the solutions became extremely sensitive to oxidation by air and became blue very rapidly. It could be shown that the enhanced oxidisability was not due to catalysis by iron salts or bromide ion, and hence must be ascribed to a new ionic species in the iridium III solutions. As the acid concentration of the solutions was reduced, it was found that oxidation became easier, whilst, on the other hand, if sufficient acid was present, bromine failed to effect any oxidation. These observations suggested that the easily oxidised ion is not the simple hydrated Ir^{+++} but probably an oxy or hydroxy ion of the type IrO^+ or $\text{Ir}(\text{OH})^{++}$. This ion is formed directly by the reduction of the blue oxidised solutions, or may occur by hydrolysis :



The existence of ions of this type in solution is consistent with the occurrence of basic salts such as $\text{Ir}(\text{OH})\text{SO}_4$, and the amphoteric character of the oxide, Ir_2O_3 .

When titrated potentiometrically with cerium IV salts or potassium permanganate the resulting curves showed an initial very sharp rise in the potential

due to the oxidation of Ir^{III} to Ir^{IV} , followed by the usual flattening and a sharp potential increase at approximately 1.27 volts. This signalled the end of the reaction $\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}} + e'$, and the commencement of the reaction $\text{Ir}^{\text{IV}} \rightarrow \text{Ir}^{\text{VI}} + 2e'$. The latter reaction was incomplete at the maximum potential available from the oxidising agent.

However, if the oxidised solutions were reduced with ferrous sulphate quite different curves were obtained, showing three potential breaks. The additional

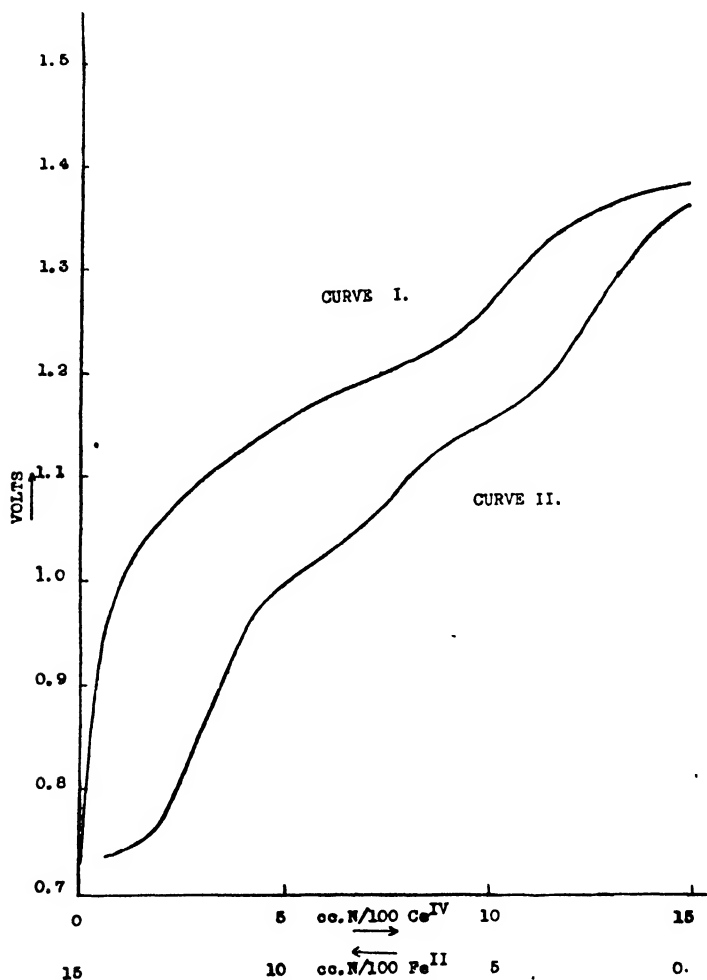


Fig. 1.

end point occurring at approximately 1.1 volts, as will be shown later, is not due to reduction of Ir^{VI} to the unknown valency state Ir^{V} , but to an unstable form of Ir^{IV} , which arises only by reduction of Ir^{VI} and cannot be obtained by oxidation of Ir^{III} (Curves I, II).

The anodic oxidation of iridium III salts in nitric, perchloric and sulphuric acids gave progressively green, blue, violet, brown violet and finally brown solutions. The last stage, which involved the formation of an iridium VI compound, could be reached only in acid concentrations above 3 normal, with high current densities on a clean polished platinum anode. In solutions of

lower acidity the anode became covered with a brownish blue deposit of (presumably) iridium trioxide and the oxidation of the solution stopped at the violet stage of iridium IV, which was also the ultimate oxidation that could be achieved with low current densities, or roughened electrodes.

It is significant that the brownish deposit on the anode was not formed in strongly acid solution, and it is suggested that, in the presence of sufficient acid, the oxide IrO_3 may react to form salts of the cation IrO_2^{++}

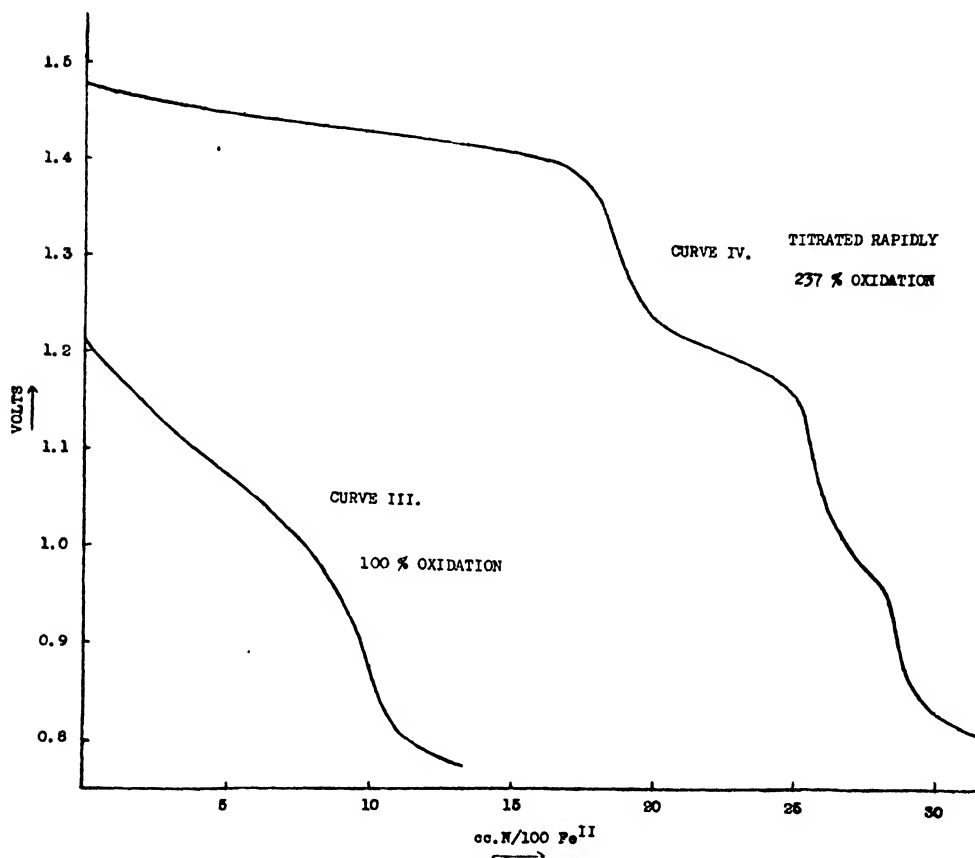
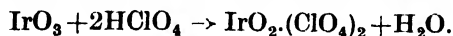


Fig. 2.

Such salts are analogous to the osmyl salts $\text{OsO}_3 \cdot \text{X}_2$, and the well known uranyl salts $\text{UO}_3 \cdot \text{X}_2$.

When the violet solutions were titrated potentiometrically with ferrous sulphate solution, the curves showed only one step due to the reduction of iridium IV to iridium III (Curve III). The brown solutions, when titrated rapidly, gave curves showing three steps; but, if titrated very slowly, only two steps (Curves IV, V). From the total percentage oxidation of the brown solutions and the width of each of the steps (i.e. the titration value), it could be shown that the first reduction step, in the rapidly titrated solutions, was from iridium VI to an unstable form of iridium IV, and not to the unknown valency state of five; the second, the reduction of the unstable form of iridium IV to iridium III; and the last step, the reduction of the stable form of iridium IV

to iridium III. In the slow titration, the potential break at the end of the reduction of iridium VI was very much larger, and the step due to the reduction of the unstable form of iridium IV disappeared.

Provided that the oxidation was not carried beyond 100 per cent. (i.e. Ir^{IV}) the unstable form of iridium IV could not be detected on the curves, and where the oxidation was carried to the hexavalent stage, the width of the step due to the unstable form was proportional to the amount of iridium VI present. It is concluded, therefore, that the unstable tetravalent state can only arise by reduction of the hexavalent state. The maximum oxidation achieved in these experiments was 273 per cent.

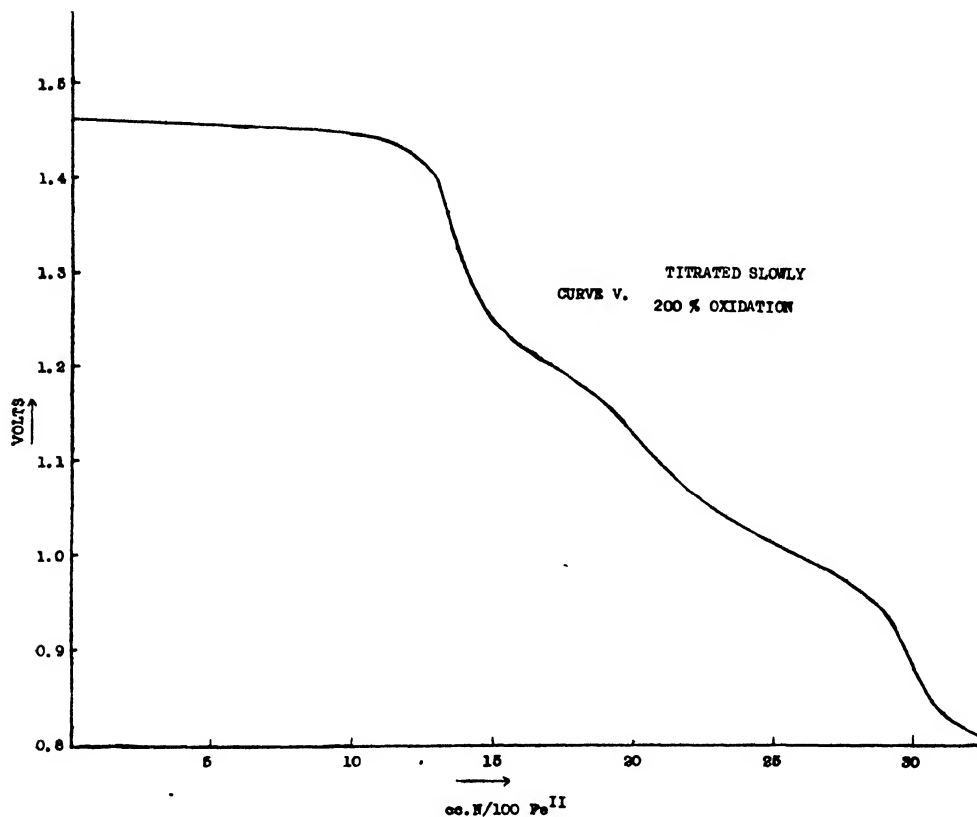
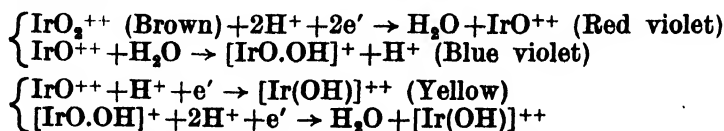
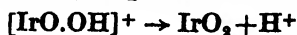


Fig. 3.

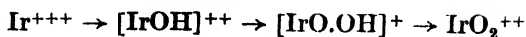
If the assumption is made that the unstable form of quadrivalent iridium carries the larger charge, and then the charge is reduced by hydrolysis to the stable form of the quadrivalent state, the following scheme is consistent with the results obtained.



In weakly acid solutions the blue violet solutions of the stable form of quadrivalent iridium yield a very fine precipitate of iridium dioxide.



The oxidation from Ir^{III} proceeds



Although dark violet blue solid crystalline substances have been obtained by the oxidation of iridium III nitrate, sulphate and perchlorate, none of the preparations has been obtained in a pure state. The work on the isolation of these compounds is proceeding.

In a subsequent paper the redox potentials of the Ir^{III}/Ir^{IV} and Ir^{IV}/Ir^{VI} couples will be discussed.

EXPERIMENTAL.

Iridium III Salt Solutions.

Potassium hexachloriridate IV (1.2 g.) was dissolved in 50 ml. of water at 80° C. and whilst hot treated with sodium hydroxide solution (0.40 g. in 50 ml. of water). The mixture was adjusted with dilute alkali until faintly alkaline, and maintained near the boiling point to cause the blue precipitate of hydrated iridium dioxide to granulate. This was removed by centrifuging, washed with hot water until it commenced to peptise and then dissolved by heating with a mixture of 20% sulphuric acid (20 ml.), 5% sulphurous acid (20 ml.), and water (30 ml.). The mixture was boiled down to half the volume to expel all sulphur dioxide, and the greenish blue solution of iridium III sulphate centrifuged to remove traces of undissolved iridium IV and iridium III oxides.

The solution of the sulphate was diluted to 50 ml. with water, and, keeping the temperature below 40° C., cold 10% sodium hydroxide was added until the initial precipitate of iridium III basic sulphate and hydroxide was just dissolved. The greenish yellow solution of sodium iridate III was cooled to room temperature, and the pH adjusted to approximately 6.5 with dilute sulphuric acid. The yellowish precipitate was centrifuged and washed once with cold water. By dissolving in cold normal sulphuric acid and making the volume to 200 ml. an approximately 0.01 M solution of the sulphate resulted.

The iridium III perchlorate was made in the same way, using normal perchloric acid to dissolve the precipitate. The hydroxide was reprecipitated with sodium hydroxide and redissolved. The last traces of sulphates were removed by the addition of a few drops of barium perchlorate solution. The nitrate was prepared the same way. All of the solutions became greenish and finally blue on standing. The nitrate became very dark blue in a few hours.

The iridium content in all solutions was found by evaporation of a known volume to dryness, followed by ignition to the metal. Traces of sodium salts were washed from the ignited metal with hot dilute hydrochloric acid.

The Potentiometric Oxidation of Iridium III Salts.

The potentiometric set-up was similar to that used in previous work (Dwyer, Nyholm and McKenzie, 1944). The mixture at 25° C. was stirred mechanically in a current of purified carbon dioxide during the titration with approximately N/100 potassium permanganate, cerium IV sulphate, nitrate or perchlorate as oxidising agents, or ferrous sulphate for the back titration of the oxidised solutions. In all titrations the initially yellow or greenish yellow solutions became green, blue and finally bluish violet. In the back titration, except in strongly acid solutions, these colour changes were not entirely reversed, and a pale blue colloidal suspension of iridium dioxide was left at the end.

Substantially the same results were obtained with all of the oxidising agents, at acid concentrations from 0.5 N to 6 N, showing a potential break at approximately 1.27 volts. From the volume of oxidising agent used, this corresponded to the end of the oxidation $\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}$. (Curve I.) Further addition of oxidising agent involved only partial oxidation to the hexavalent state.

The reduction curves with ferrous sulphate gave typical curves involving potential breaks at 1.27 volts, 1.1 volts and 0.9 volt. The break at 1.1 volts was usually poorly defined.

The Anodic Oxidation.

The anodic oxidation cell consisted of a small beaker (30 ml.) containing a cylinder of smooth polished platinum, which fitted the beaker so closely that the inner side of the cylinder could be considered as the effective anode surface. A small sintered glass crucible with the base removed, and fitting loosely into the platinum cylinder, contained the platinum wire cathode. The solution to be oxidised containing the appropriate amount of acid was placed in the beaker, and the cathode chamber was filled with acid of the same concentration; the levels in the two chambers being adjusted so that the cathode level was slightly higher. The solution being oxidised was stirred with a rapid stream of fine carbon dioxide bubbles. When oxidation was complete, the cathode was removed, the porous membrane washed out by allowing some of the cathode liquid to percolate through; then the rest of the cathode acid added, and the anode washed with a little further acid. The solution was then made up to a specified volume.

The percentage oxidation achieved was determined by taking a known volume of solution, diluting with water, adding excess potassium iodide, and titrating the liberated iodine with sodium thiosulphate. From the known iridium content of the solution before oxidation, the calculation can then be made. A small correction was necessary for the iridium deposited on the cathode.

In the sulphate solutions, persulphate was formed during the oxidation making the estimation of the percentage oxidation impossible, whilst the nitric acid in the nitrate solutions interfered with the titration by slowly liberating iodine. For these reasons, beyond qualitatively establishing that the same products are formed in sulphate and nitrate solutions, the work has been restricted to the perchlorate.

It was found that provided the current was more than 0.2 amp. (6 V. applied), or the current density of more than 2.6×10^{-3} amp./sq. cm., the extent of oxidation was a function of the time and the state of the electrode surface. With roughened electrodes, or electrodes that had been used previously without cleaning, gassing occurred and the oxidation could not be carried much beyond the Ir^{IV} state. The electrode between experiments was cleaned by making it the anode in 5 N sulphuric acid and passing a current of 4–5 amps. for twenty minutes. Table I shows the results obtained by oxidising in 4 N perchloric acid with a current of 0.5 amp. (6.5×10^{-3} amp./sq. cm. of anode surface).

TABLE I.
0.0150 gm. of Ir in 10 ml. solution.

| Time in Minutes. | Loss on Cathode. Grammes. | Total Ir. Grammes. | N/100 $\text{Na}_2\text{S}_2\text{O}_3$. Millilitres. | Percentage Oxidation. | Percentage Ir^{VI} . |
|------------------|---------------------------|--------------------|--|-----------------------|--------------------------------------|
| 10 | 0.0006 | 0.0144 | 15.9 | 110 | 5.0 |
| 20 | 0.0012 | 0.0138 | 24.2 | 175 | 37.5 |
| 40 | 0.0022 | 0.0128 | 27.4 | 214 | 57.0 |
| 90 | 0.0029 | 0.0121 | 29.3 | 242 | 71.0 |

The potentiometric reduction of the anodically oxidised solutions was carried out in the assembly described above, with approximately N/100 ferrous sulphate solution. Typical reduction curves of solutions oxidised to various stages are shown in Figures 1 to 3.

SUMMARY.

The oxidation of iridium III sulphate, perchlorate and nitrate with potassium permanganate, or cerium IV salts yields bluish violet solutions, which probably contain the cation $[\text{IrO.OH}]^+$. The anodic oxidation yields bluish violet solutions, which contain the same ion, or the oxidation can be carried to the stage of iridium VI, which exists in the solution as the brown ion IrO_2^{++} .

By examination of the potentiometric reduction curves of the brown solutions, it is concluded that an unstable form of quadrivalent iridium, probably

as the reddish violet ion IrO^{++} , is the first reduction product of the ion IrO_3^{++} . The unstable ion rapidly changes to the stable $[\text{IrO.OH}]^+$, and can be obtained only by the reduction of iridium VI.

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PHYSICAL INVESTIGATIONS ON COMPLEXES OF DIPHENYLTHIOCARBAZONE.

By L. E. MALEY, M.Sc.,

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University of Sydney.*

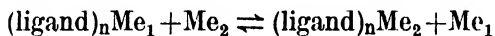
Manuscript received, August 16, 1950. Read, October 4, 1950.

The object of this investigation was to study the interaction of metal complexes of diphenylthiocarbazone with metal ions, in order that information concerning the strength of the binding of the metal to the ligand, diphenylthiocarbazone, and the extent of the exchange between metal ions in solution with metal atoms bound to this ligand could be obtained.

Previous investigations by Maley and Mellor (1949) on the stability of a series of metal complexes have shown that the order of the stability constants for metal chelates with a series of ligands was independent of the chelating organic molecules investigated.

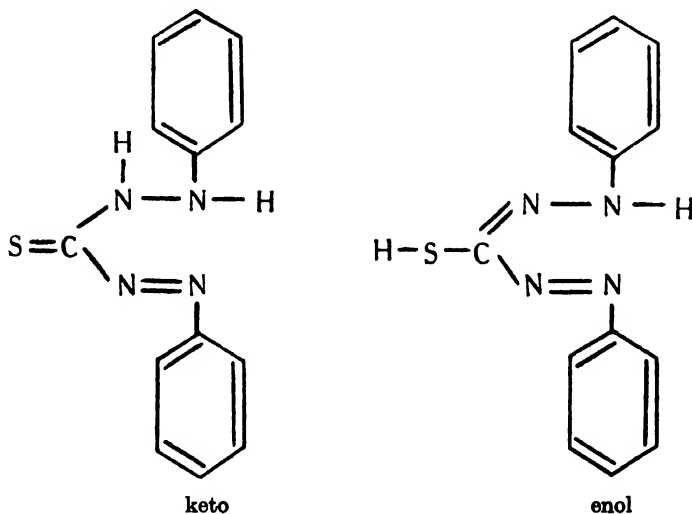
If one metal complex is more stable than another of the same type, it should be possible under suitable conditions for one metal to displace another metal from a less stable complex.

The reaction



should therefore proceed and displace the original metal Me_1 from its complex if Me_2 forms a more stable complex with the ligand.

Diphenylthiocarbazone, which is acidic in character and forms chelates with many metals, exists in both the keto and enol form.



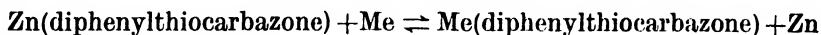
According to Fisher (1934) the keto form reacts with metal ions. The imino hydrogen atom is replaced by the metal atom, which is then coordinatively bound to the nitrogen. These complexes are soluble in organic solvents and as a rule are coloured.

The reagent diphenylthiocarbazone is itself insoluble in water and dilute mineral acids but is soluble in chloroform, carbon tetrachloride, and alcohol.

A chloroform mixture of the uncombined chelate and the chelate combined with the metal ion can be separated by a dilute aqueous ammonia solution (0.02 M), which extracts the uncombined complex diphenylthiocarbazone leaving the pure colour of the metal complex in the chloroform layer.

METHOD OF INVESTIGATION OF THE REACTION.

In the present investigation the following specific exchange reactions were studied :



where Me = Cu, Co and Zn.

The extent to which this reaction proceeds from left to right was noted by using radioactive ions. The zinc atoms in each case were labelled by using radioactive zinc solutions.

The reagent, diphenylthiocarbazone, which is a spot reagent and used for determining metal ions in concentrations 1γ to 100γ, is very sensitive to trace metal ions and this factor necessitated the taking of special precautions to ensure that all apparatus and reagents were free of zinc and other trace metals before proceeding.

EXPERIMENTAL.

Reagents.

Diphenylthiocarbazone B.D.H. quality was used throughout and found free of oxidised products.

Trace elements were eliminated from the pyrex glassware by thorough cleaning, washing and testing it with diphenylthiocarbazone reagent until free of metal ions. No grease or lubricant (other than water) or rubber fittings could be used on the separating funnels as all these were found to contain a significant amount of zinc.

The distilled water and absolute alcohol and ammonia were redistilled several times in pyrex glassware and the chloroform purified by distilling under a cover of aqueous solution of sodium thiosulphate containing a little NaOH, drying the distillate over CaCl₂ and redistilling.

Preparation of Zinc Diphenylthiocarbazone.

It was prepared by adding diphenylthiocarbazone chloroform reagent (15 milligrammes in 100 ml. CHCl₃) to the dilute 50γ aqueous zinc chloride at pH 7.0. The excess reagent was removed by extracting it with dilute (0.02 M) aqueous ammonia until the upper layer was water clear.

The red complex remains in the chloroform layer. It was made up as required because the colour fades on standing due to slow oxidation.

The formation of metal diphenylthiocarbazone is influenced by the hydrogen ion concentration of the aqueous solution [Fisher and Leopoldi (1934), Fisher (1934), Hibbard (1937), White (1936)].

The percentage of zinc ions extracted from an aqueous solution by a chloroform diphenylthiocarbazone solution varies considerably with pH. The partition effect in dilute solutions is illustrated by Fig. 1 (Hibbard, 1937).

The exchange reactions were therefore carried out experimentally at the constant pH of 7.0.

Alcoholic zinc diphenylthiocarbazone was prepared by evaporating the chloroform solution to a low bulk and then diluting with absolute alcohol giving a one-phase solution.

Exchange Reactions.

The alcohol zinc diphenylthiocarbazone was mixed with approximately an equal volume of solution of the metal salt solution at the same molar concentration and at pH 7.0, so that

$$\frac{[\text{Zinc complex}]}{[\text{Metal salt conc.}]} \sim 1$$

The zinc complex was then separated from the metal solution by adding CHCl_3 . The CHCl_3 layer was washed with water and the water layer washed with CHCl_3 . Both layers were then diluted, an aliquot portion taken, evaporated and dried on a glass counting plate and their respective radioactivity measured on a Geiger Muller counter with a scale of eight using a β tube with a two-inch lead shielding and a thin mica window.

No self adsorption corrections were needed due to the relative high energy of the β and γ rays emitted from $\text{Zn}^* 65$ used, and, due to its relatively long half life of 250 days, no decay corrections were required.

Due to the fact that emission of radioactive radiations follow statistical laws of random processes the statistical probable error in the recorded activity is given by Poisson's Term, $0.6745\sqrt{A^1}$, where A^1 is the number of events recorded.

The activity of the sample was then determined as follows :

$$\text{Average sample + background count} = B \pm 0.6745 \sqrt{B}$$

$$\text{Average sample count} = B - A \pm \sqrt{(0.6745 \sqrt{B})^2 + (0.6745 \sqrt{A})^2}$$

where A is the average background count.

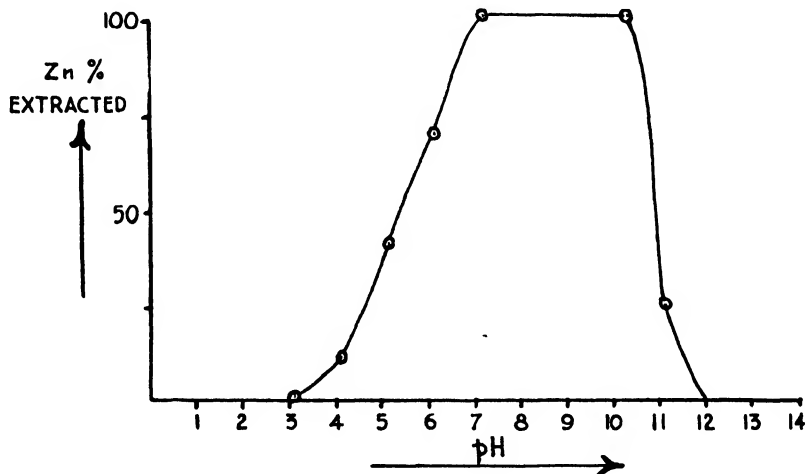


Fig. 1

The concentration of the metal ions in the aqueous phase was determined by separating the water layer, converting it into the diphenylthiocarbazone complex in chloroform and using a Klett photometer to determine its concentration.

In the copper and cobalt exchange reactions copper sulphate and cobalt nitrate solutions were added to the zinc complex solutions and allowed to stand several hours. The separation was then effected as above by adding chloroform and the activities of the two layers were measured. In both cases the activity of the aqueous solution increased to 100% of the original complex activity, indicating a complete exchange of the zinc atoms in the complex with the copper and cobalt ions.

The reaction between zinc atoms in the complex and zinc ions in solution was studied in the first instance by using active complex and inactive zinc ions, and secondly inactive complex and active zinc ions.

The relative concentrations of the zinc in both layers were then compared with the corresponding activities and were found to agree.

The exchange rate for the zinc-zinc exchange was very rapid in the alcoholic aqueous solution and within the minimum time required to separate the solutions $\frac{1}{2}$ to 1 minute the activity of the aqueous layer reached 50% of the total activity, which means there is a 100% exchange of the zinc ions in solution with zinc atoms in the complex.

ACKNOWLEDGEMENTS.

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SUMMARY.

There is a rapid exchange between zinc ions in solution with zinc atoms in zinc diphenylthiocarbazon and the zinc atoms are held by relatively weak bonds to the ligand.

Copper and cobalt metals form relatively stronger bonds with the ligand and are more stable than the corresponding zinc diphenylthiocarbazon complex.

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TABLES FOR NEARLY PARABOLIC ELLIPTIC MOTION.*

By HARLEY WOOD, M.Sc.

Manuscript received, February 20, 1950. Read, November 1, 1950.

In this article tables are given for the representation of nearly parabolic elliptic Keplerian motion based on the formulæ of a previous paper (Wood, 1950a).

Equation (9) of that paper may be written

$$D_1 = 6k(1+e)^{3/2}q^{-3/2}t = (1+e)6\mu + \mu^3 6 \left\{ \frac{\sin^{-1}\epsilon^{1/2}\mu - \epsilon^{1/2}\mu}{\epsilon^{3/2}\mu^3} \right\}, \dots\dots\dots (1)$$

where k is the Gaussian constant, e the eccentricity, $\epsilon = (1-e)/(1+e)$, $\mu = y_0/q$, $\lambda = x_0/q$ and x_0, y_0 are the rectangular coordinates in the plane of motion with the x_0 axis directed towards perihelion. When the place in the orbit is known, and hence one of the alternatives

$$\mu = (\sin E)/\epsilon^{1/2} = y_0/q = (r \sin v)/q$$

calculable, this formula may be used to calculate perihelion time. The coefficient of μ^3 ,

$$6 \left\{ \frac{\sin^{-1}\epsilon^{1/2}\mu - \epsilon^{1/2}\mu}{\epsilon^{3/2}\mu^3} \right\} = A$$

is given in Table 1 with argument $\epsilon^{1/2}\mu$. The table was calculated to nine decimal places using the series when $\epsilon^{1/2}\mu \leq 0.20$ and thereafter the *Table of Arc sin x* prepared by the "Mathematical Tables Project" (1945). The values of A , and the remaining functions of this article, were calculated at ten times the interval given and then sub-tabulated to the interval of the table, the intention being that errors should not exceed 0.52 unit of the last recorded place.

In order to provide for iterative computation of μ from equation (1) and of velocities facilities are given for convenient calculation of

$$\begin{aligned} \frac{dD_1}{d\mu} &= 6(1+e) + \frac{6}{\epsilon} \left\{ \frac{1}{(1-\epsilon\mu^2)^{1/2}} - 1 \right\} \\ &= 6(1+e) + \mu^2 6 \left\{ \frac{1 - (1-\epsilon\mu^2)^{1/2}}{\epsilon\mu^2(1-\epsilon\mu^2)^{1/2}} \right\}. \\ I &= 6 \left\{ \frac{1 - (1-\epsilon\mu^2)^{1/2}}{\epsilon\mu^2(1-\epsilon\mu^2)^{1/2}} \right\} \end{aligned}$$

is given in Table 1 and a correction to an approximate value of μ may be obtained by the formula

$$\Delta\mu = \{D_1 - 6(1+e)\mu - A\mu^3\} / \{6(1+e) + I\mu^2\}. \dots\dots\dots (2)$$

* This paper is printed with the aid of a grant from the Commonwealth Scientific Publications Committee.

For obtaining μ from the known elements of the orbit tables are given for the use of formulæ (23) of the previous paper. Repeating these in a form adapted to the present purpose we have

$$D = [12k(1+e)^{1/2}q^{-3/2}c]t$$

where

$$c^2 = 1 + \gamma_1 \epsilon + \gamma_2 \epsilon^2 + \dots,$$

$12k = 0.2064\ 2519$, c is obtained from Table 2 and the coefficient of t in the square brackets can be computed for the whole orbit.

Also

$$D = 12c\sigma + c^3\sigma^3 \dots\dots\dots (3)$$

and

$$\mu = \sigma \left\{ \begin{array}{l} 1 + g_{12}\epsilon\sigma^2 + g_{22}\epsilon^2\sigma^2 + g_{32}\epsilon^3\sigma^2 + \dots\dots \\ \quad + g_{24}\epsilon^2\sigma^4 + g_{34}\epsilon^3\sigma^4 + \dots\dots \\ \quad + g_{36}\epsilon^3\sigma^6 + \dots\dots \end{array} \right\}$$

Now writing

$$J = 1 + g_{12}\epsilon\sigma^2 + g_{24}\epsilon^2\sigma^4 + g_{36}\epsilon^3\sigma^6 + \dots,$$

$$h = \epsilon + \frac{g_{32}}{g_{22}}\epsilon^2 + \frac{g_{42}}{g_{22}}\epsilon^3 + \dots$$

and

$$-K = g_{22}\epsilon\sigma^2 + g_{34}\epsilon^2\sigma^4 + g_{46}\epsilon^3\sigma^6 + \dots$$

we have

$$\mu = \frac{c\sigma}{c} \{J - hK + R\}, \dots\dots\dots (4)$$

where R is a function of ϵ and μ defined by the equation.

Inserting the values of the coefficients we have

$$c^2 = 1 - 0.8\epsilon - 0.03428\ 57143\epsilon^2 - 0.01980\ 9524\epsilon^3 - 0.01323\ 4385\epsilon^4 \\ - 0.00963\ 4\epsilon^5 - 0.00742\epsilon^6 - 0.0059\epsilon^7,$$

$$J = 1.0 - 0.15\epsilon\sigma^2 + 0.00071\ 42857\epsilon^2\sigma^4 + 0.00003\ 96825\epsilon^3\sigma^6 \\ + 0.00000\ 24930\epsilon^4\sigma^8 + 0.00000\ 01683\epsilon^5\sigma^{10},$$

$$K = +0.00285\ 7143\epsilon\sigma^2 - 0.00112\ 6984\epsilon^2\sigma^4 - 0.00005\ 1252\epsilon^3\sigma^6 \\ - 0.00000\ 2454\epsilon^4\sigma^8 - [0.000033\epsilon^5\sigma^{10}],$$

$$h = 1.0\epsilon + 0.57777\ 7778\epsilon^2 + 0.38600\ 2886\epsilon^3 + 0.28097\ 7689\epsilon^4 \\ - [2.2\epsilon^5],$$

where the terms in the brackets are not determined like the others but are empirical terms added to reduce the value of R . Their greatest effect on hK within the range of the table is 40 units in the ninth decimal place. Using the manuscript tables calculated from the above series to two places beyond what is recorded here, values of R were calculated from equation (4), μ first having been obtained from equation (2). The "Table of Values of R " gives the values found in units of the ninth decimal place, including errors of computation up to two units involved in using the full nine figures. R is negligible in seven figure work.

Table of Values of R in Units of the Ninth Decimal Place.

| $\epsilon \backslash \epsilon^{1/2}\sigma$ | 0.02 | 0.04 | 0.06 | 0.08 | 0.10 |
|--|------|------|------|------|------|
| 0.1 | +1 | +1 | 0 | 0 | +1 |
| 0.2 | 0 | +1 | +1 | 0 | -2 |
| 0.3 | 0 | 0 | +1 | 0 | -2 |
| 0.4 | 0 | +2 | +3 | +2 | -1 |
| 0.5 | 0 | +2 | +5 | +6 | +6 |
| 0.6 | -2 | -1 | +3 | +6 | +5 |

The values of c and h are found, once for the orbit, from Table 2; $c\sigma$ is obtained from equation (3) using tables of parabolic motion (Wood, 1950b), and J and K come from Table 3 with argument $[\epsilon^{1/2}c^{-1}]c\sigma$. When second differences are appreciable they may be allowed for by using the table with argument n and $\Delta_0'' + \Delta_1''$, published in the *Nautical Almanac for 1937* and reprinted in the *Interpolation and Allied Tables*.

Having μ , we require

$$\lambda = 1 - \frac{1}{2(1+e)}\mu^2 \left\{ \frac{2 - 2(1 - \epsilon\mu^2)^{1/2}}{\epsilon\mu^2} \right\},$$

which is equation 6 of the first paper. The quantity

$$\frac{2 - 2(1 - \epsilon\mu^2)^{1/2}}{\epsilon\mu^2} = N$$

is given in Table 1 with argument $\epsilon^{1/2}\mu$.

The formulae for the rectangular equatorial heliocentric coordinates are then

$$x = [A_x] - \left[\frac{A_x}{2(1+e)} \right] N\mu^2 + [B_x]\mu,$$

$$y = [A_y] - \left[\frac{A_y}{2(1+e)} \right] N\mu^2 + [B_y]\mu,$$

$$z = [A_z] - \left[\frac{A_z}{2(1+e)} \right] N\mu^2 + [B_z]\mu,$$

where A_x, B_x, \dots have the same meaning as in the second paper (Wood, 1950b) and the coefficients in the square brackets are precomputed.

As an illustration, using the conventional example from Gauss' *Theoria Motus*, we take

$$e = 0.9676 \ 4567,$$

$$v = 100^\circ,$$

$$\mu = (r \sin v)/q = 2.3291 \ 134.$$

$$q = 0.5829 \ 751,$$

$$\tan v = -5.671282,$$

The preliminary calculations of the constants required to compute either perihelion time or an ephemeris place give

$$\epsilon = 0.0164 \ 4317,$$

$$\epsilon^{1/2} = 0.1282 \ 309,$$

$$c = 0.9933 \ 962,$$

$$\epsilon^{1/2}c^{-1} = 0.1290 \ 833,$$

$$6k(1+e)^{3/2}q^{-3/2} = 0.6399 \ 971,$$

$$6(1+e) = 11.8058 \ 740,$$

$$12k(1+e)^{1/2}q^{-3/2}c = 0.6462 \ 248,$$

$$h = 0.01660.$$

For calculation of perihelion time we obtain

$$\begin{aligned}\varepsilon^{1/2}\mu &= 0.2986\ 643, & A &= 1.0424\ 100, \\ t &= 63.54399\ \text{days}.\end{aligned}$$

A many-figure calculation gives $t=63.5439\ 858$ days.

In calculating an ephemeris place with $t=63.543986$ days we obtain

$$\begin{aligned}c\sigma &= 2.3459\ 994, & \mu &= 2.3291\ 135, \\ \varepsilon^{1/2}\sigma &= 0.3028\ 293, & \varepsilon^{1/2}\mu &= 0.2986\ 643, \\ J &= 0.9862\ 502, & N &= 1.0233\ 538, \\ K &= 0.0002\ 525, & \lambda &= -0.4106\ 856\end{aligned}$$

and for comparison with the original data we give

$$\tan v = \mu/\lambda = -5.671281, \quad r = 100^\circ\ 00'\ 00''.01.$$

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 Wood, H., 1950a. THIS JOURNAL, 83, 150. Also Sydney Obs. Papers No. 10.
 ————1950b. THIS JOURNAL, 83, 181. Also Sydney Obs. Papers No. 11.
-

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|-------------------------|-------------------|-------------------------|-----------------------------|-------------------------|-------------------|-------------------------|
| | 1. | 3. | 1. | | 1. | 3. | 1. |
| 0.000 | 0000 000 | 9000 | 0000 000 | 0.050 | 0011 267 | 0056 | 0006 258 |
| 0.001 | 0000 004 ⁴ | 0000 ⁰ | 0000 002 ² | 0.051 | 0011 723 ⁴⁵⁶ | 0059 ³ | 0006 511 ²⁵³ |
| 0.002 | 0000 018 ¹⁴ | 0000 ⁰ | 0000 010 ⁸ | 0.052 | 0012 188 ⁴⁶⁶ | 0061 ² | 0006 769 ²⁶⁸ |
| 0.003 | 0000 041 ²³ | 0000 ⁰ | 0000 022 ¹² | 0.053 | 0012 662 ⁴⁷⁴ | 0063 ² | 0007 032 ²⁶³ |
| 0.004 | 0000 072 ³¹ | 0000 ⁰ | 0000 040 ¹⁸ | 0.054 | 0013 145 ⁴⁸³ | 0066 ³ | 0007 301 ²⁶⁹ |
| | | | | | | | |
| 0.005 | 0000 113 | 0001 ⁰ | 0000 062 | 0.055 | 0013 637 | 0068 ³ | 0007 574 ²⁷⁸ |
| 0.006 | 0000 162 ⁴⁹ | 0001 ⁰ | 0000 090 ²⁸ | 0.056 | 0014 138 ⁵⁰¹ | 0071 ³ | 0007 852 ²⁸⁴ |
| 0.007 | 0000 221 ⁵⁹ | 0001 ⁰ | 0000 122 ³² | 0.057 | 0014 649 ⁵¹¹ | 0073 ² | 0008 136 ²⁸⁸ |
| 0.008 | 0000 288 ⁶⁷ | 0001 ⁰ | 0000 160 ³⁸ | 0.058 | 0015 168 ⁵¹⁹ | 0076 ³ | 0008 424 ²⁸⁸ |
| 0.009 | 0000 365 ⁷⁷ | 0002 ¹ | 0000 203 ⁴³ | 0.059 | 0015 697 ⁵²⁹ | 0079 ² | 0008 718 ²⁹⁴ |
| | | | | | | | |
| 0.010 | 0000 450 | 0002 ¹ | 0000 250 ⁵³ | 0.060 | 0016 235 ⁵⁴⁷ | 0081 ³ | 0009 016 ³⁰⁴ |
| 0.011 | 0000 545 ⁹⁵ | 0003 ⁰ | 0000 303 ⁵⁷ | 0.061 | 0016 782 ⁵⁵⁶ | 0084 ³ | 0009 320 ³⁰⁹ |
| 0.012 | 0000 648 ¹⁰³ | 0003 ¹ | 0000 360 ⁶⁷ | 0.062 | 0017 338 ⁵⁶⁵ | 0087 ³ | 0009 629 ³¹³ |
| 0.013 | 0000 761 ¹¹³ | 0004 ⁰ | 0000 423 ⁶³ | 0.063 | 0017 903 ⁵⁷⁴ | 0090 ² | 0009 942 ³¹⁹ |
| 0.014 | 0000 882 ¹²¹ | 0004 ¹ | 0000 490 ⁶⁷ | 0.064 | 0018 477 ⁵⁸³ | 0092 ³ | 0010 261 ³²⁴ |
| | | | | | | | |
| 0.015 | 0001 013 ¹³⁹ | 0005 ¹ | 0000 563 ⁷⁷ | 0.065 | 0019 060 ⁵⁹³ | 0095 ³ | 0010 585 ³²⁹ |
| 0.016 | 0001 152 ¹⁴⁹ | 0006 ⁰ | 0000 640 ⁸³ | 0.066 | 0019 653 ⁶⁰² | 0098 ³ | 0010 914 ³³⁴ |
| 0.017 | 0001 301 ¹⁵⁷ | 0006 ¹ | 0000 723 ⁸⁷ | 0.067 | 0020 255 ⁶¹⁰ | 0101 ³ | 0011 248 ³³⁹ |
| 0.018 | 0001 458 ¹⁶⁷ | 0007 ¹ | 0000 810 ⁹³ | 0.068 | 0020 865 ⁶²⁰ | 0104 ³ | 0011 587 ³⁴⁴ |
| 0.019 | 0001 625 ¹⁷⁵ | 0008 ¹ | 0000 903 ⁹⁷ | 0.069 | 0021 485 ⁶³⁰ | 0108 ⁴ | 0011 931 ³⁴⁹ |
| | | | | | | | |
| 0.020 | 0001 800 | 0009 ¹ | 0001 000 ¹⁰³ | 0.070 | 0022 115 ⁶³⁸ | 0111 ³ | 0012 280 ³⁵⁴ |
| 0.021 | 0001 985 ¹⁸⁵ | 0010 ¹ | 0001 103 ¹⁰⁷ | 0.071 | 0022 753 ⁶⁴⁷ | 0114 ³ | 0012 634 ³⁶⁰ |
| 0.022 | 0002 179 ²⁰² | 0011 ¹ | 0001 210 ¹¹³ | 0.072 | 0023 400 ⁶⁵⁷ | 0117 ³ | 0012 994 ³⁶⁴ |
| 0.023 | 0002 381 ²¹² | 0012 ¹ | 0001 323 ¹¹⁷ | 0.073 | 0024 057 ⁶⁶⁶ | 0120 ³ | 0013 358 ³⁷⁰ |
| 0.024 | 0002 593 ²²¹ | 0013 ¹ | 0001 440 ¹²³ | 0.074 | 0024 723 ⁶⁷⁵ | 0124 ⁴ | 0013 728 ³⁷⁴ |
| | | | | | | | |
| 0.025 | 0002 814 ²²⁹ | 0014 ¹ | 0001 563 ¹²⁸ | 0.075 | 0025 398 | 0127 ⁴ | 0014 102 ³⁸⁰ |
| 0.026 | 0003 043 ²³⁹ | 0015 ¹ | 0001 691 ¹³² | 0.076 | 0026 082 ⁶⁸⁴ | 0131 ⁴ | 0014 482 ³⁸⁵ |
| 0.027 | 0003 282 ²⁴⁸ | 0016 ² | 0001 823 ¹³⁸ | 0.077 | 0026 775 ⁶⁹³ | 0134 ⁴ | 0014 867 ³⁸⁹ |
| 0.028 | 0003 530 ²⁵⁶ | 0018 ² | 0001 961 ¹⁴² | 0.078 | 0027 478 ⁷⁰³ | 0138 ⁴ | 0015 256 ³⁹⁵ |
| 0.029 | 0003 786 ²⁶⁶ | 0019 ¹ | 0002 103 ¹⁴⁸ | 0.079 | 0028 189 ⁷¹¹ | 0141 ⁴ | 0015 651 ⁴⁰⁰ |
| | | | | | | | |
| 0.030 | 0004 052 ²⁷⁵ | 0020 ² | 0002 251 ¹⁵³ | 0.080 | 0028 910 ⁷³⁰ | 0145 ⁴ | 0016 051 ⁴⁰⁶ |
| 0.031 | 0004 327 ²⁸⁴ | 0022 ² | 0002 404 ¹⁵⁷ | 0.081 | 0029 640 ⁷⁴⁰ | 0148 ⁴ | 0016 457 ⁴¹⁰ |
| 0.032 | 0004 611 ²⁹³ | 0023 ² | 0002 561 ¹⁶³ | 0.082 | 0030 380 ⁷⁴⁸ | 0152 ⁴ | 0016 867 ⁴¹⁵ |
| 0.033 | 0004 904 ³⁰² | 0025 ² | 0002 724 ¹⁶⁸ | 0.083 | 0031 128 ⁷⁵⁸ | 0156 ⁴ | 0017 282 ⁴²¹ |
| 0.034 | 0005 206 ³¹¹ | 0026 ² | 0002 892 ¹⁷² | 0.084 | 0031 886 ⁷⁶⁷ | 0160 ⁴ | 0017 703 ⁴²⁵ |
| | | | | | | | |
| 0.035 | 0005 517 | 0028 ¹ | 0003 064 ¹⁷⁸ | 0.085 | 0032 653 ⁷⁷⁶ | 0164 ⁴ | 0018 128 ⁴³¹ |
| 0.036 | 0005 836 ³¹⁹ | 0029 ¹ | 0003 242 ¹⁸³ | 0.086 | 0033 429 ⁷⁸⁶ | 0167 ⁴ | 0018 559 ⁴³⁵ |
| 0.037 | 0006 166 ³³⁰ | 0031 ² | 0003 425 ¹⁸⁸ | 0.087 | 0034 215 ⁷⁹⁴ | 0171 ⁴ | 0018 994 ⁴⁴¹ |
| 0.038 | 0006 504 ³⁴⁷ | 0033 ² | 0003 613 ¹⁹² | 0.088 | 0035 009 ⁸⁰⁴ | 0175 ⁴ | 0019 435 ⁴⁴⁶ |
| 0.039 | 0006 851 ³⁵⁶ | 0034 ² | 0003 805 ¹⁹⁸ | 0.089 | 0035 813 ⁸¹⁴ | 0179 ⁴ | 0019 881 ⁴⁵¹ |
| | | | | | | | |
| 0.040 | 0007 207 | 0036 ² | 0004 003 ²⁰³ | 0.090 | 0036 627 ⁸²² | 0183 ⁵ | 0020 332 ⁴⁵⁷ |
| 0.041 | 0007 572 ³⁶⁵ | 0038 ² | 0004 206 ²⁰⁸ | 0.091 | 0037 449 ⁸³² | 0188 ⁵ | 0020 789 ⁴⁶¹ |
| 0.042 | 0007 946 ³⁷⁴ | 0040 ² | 0004 414 ²¹³ | 0.092 | 0038 281 ⁸⁴¹ | 0192 ⁴ | 0021 250 ⁴⁶⁷ |
| 0.043 | 0008 330 ³⁸⁴ | 0042 ² | 0004 627 ²¹⁸ | 0.093 | 0039 122 ⁸⁵⁰ | 0196 ⁴ | 0021 717 ⁴⁷¹ |
| 0.044 | 0008 722 ⁴⁰² | 0044 ² | 0004 845 ²²³ | 0.094 | 0039 975 ⁸⁶⁰ | 0200 ⁵ | 0022 188 ⁴⁷⁷ |
| | | | | | | | |
| 0.045 | 0009 124 | 0046 ² | 0005 068 | 0.095 | 0040 832 | 0205 ⁴ | 0022 665 ⁴⁸² |
| 0.046 | 0009 534 ⁴¹⁰ | 0048 ² | 0005 296 ²²⁸ | 0.096 | 0041 701 ⁸⁶⁹ | 0209 ⁴ | 0023 147 ⁴⁸⁷ |
| 0.047 | 0009 964 ⁴²⁰ | 0050 ² | 0005 529 ²³³ | 0.097 | 0042 579 ⁸⁷⁸ | 0213 ⁴ | 0023 634 ⁴⁹² |
| 0.048 | 0010 382 ⁴²⁸ | 0052 ² | 0005 767 ²³⁸ | 0.098 | 0043 467 ⁸⁸⁸ | 0218 ⁵ | 0024 126 ⁴⁹⁷ |
| 0.049 | 0010 820 ⁴⁴⁷ | 0054 ² | 0006 010 ²⁴³ | 0.099 | 0044 364 ⁸⁹⁷ | 0222 ⁵ | 0024 623 ⁵⁰³ |
| | | | | | | | |
| 0.050 | 0011 267 | 0056 | 0006 258 | 0.100 | 0045 270 | 0227 | 0025 126 |

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|--------------------------|-------------------|-------------------------|-----------------------------|--------------------------|--------------------|--------------------------|
| | 1. | 3. | 1. | | 1. | 3. | 1. |
| 0.100 | 0045 270 | 0227 ⁴ | 0025 126 | 0.150 | 0102 627 | 0516 ⁷ | 0056 892 |
| .101 | 0046 185 ⁹¹⁵ | 0231 ⁴ | 0025 633 ⁵⁰⁷ | .151 | 0104 019 ¹³⁹² | 0523 ⁷ | 0057 862 ⁷⁷⁰ |
| .102 | 0047 110 ⁹²⁵ | 0236 ⁵ | 0026 146 ⁵¹³ | .152 | 0105 421 ¹⁴⁰² | 0530 ⁷ | 0058 437 ⁷⁷⁵ |
| .103 | 0048 044 ⁹³⁴ | 0241 ⁵ | 0026 664 ⁵¹⁸ | .153 | 0106 832 ¹⁴¹¹ | 0537 ⁷ | 0059 218 ⁷⁸¹ |
| .104 | 0048 988 ⁹⁴⁴ | 0246 ⁵ | 0027 187 ⁵²³ | .154 | 0108 253 ¹⁴²¹ | 0544 ⁷ | 0060 004 ⁷⁸⁶ |
| | | | 529 | | | | 791 |
| 0.105 | 0049 941 ⁹⁶² | 0250 ⁵ | 0027 716 ⁵³³ | 0.155 | 0109 684 ¹⁴⁴¹ | 0552 ⁷ | 0060 795 ⁷⁹⁷ |
| .106 | 0050 903 ⁹⁸¹ | 0255 ⁵ | 0028 249 ⁵³⁹ | .156 | 0111 125 ¹⁴⁵¹ | 0559 ⁷ | 0061 592 ⁸⁰² |
| .107 | 0051 874 ⁹⁸¹ | 0260 ⁵ | 0028 788 ⁵⁴³ | .157 | 0112 578 ¹⁴⁶⁰ | 0566 ⁸ | 0062 394 ⁸⁰⁷ |
| .108 | 0052 855 ⁹⁹¹ | 0265 ⁵ | 0029 331 ⁵⁴⁹ | .158 | 0114 036 ¹⁴⁷⁰ | 0574 ⁷ | 0063 201 ⁸¹³ |
| .109 | 0053 846 ⁹⁹⁹ | 0270 ⁵ | 0029 880 ⁵⁵⁴ | .159 | 0115 508 ¹⁴⁸¹ | 0581 ⁸ | 0064 014 ⁸¹⁹ |
| 0.110 | 0054 845 ¹⁰¹⁰ | 0275 ⁵ | 0030 434 ⁵⁶⁰ | 0.160 | 0116 987 ¹⁴⁹⁰ | 0589 ⁷ | 0064 833 ⁸²³ |
| .111 | 0055 855 ¹⁰¹⁸ | 0280 ⁵ | 0030 994 ⁵⁶⁴ | .161 | 0118 477 ¹⁴⁹⁹ | 0596 ⁸ | 0065 656 ⁸²⁹ |
| .112 | 0056 873 ¹⁰²⁸ | 0285 ⁵ | 0031 558 ⁵⁷⁰ | .162 | 0119 976 ¹⁵¹⁰ | 0604 ⁸ | 0066 485 ⁸³⁵ |
| .113 | 0057 901 ¹⁰³⁷ | 0290 ⁶ | 0032 128 ⁵⁷⁵ | .163 | 0121 486 ¹⁵²⁰ | 0611 ⁸ | 0067 320 ⁸⁴⁰ |
| .114 | 0058 938 ¹⁰⁴⁷ | 0296 ⁶ | 0032 703 ⁵⁸⁰ | .164 | 0123 006 ¹⁵²⁹ | 0619 ⁸ | 0068 160 ⁸⁴⁵ |
| 0.115 | 0059 985 ¹⁰⁵⁶ | 0301 ⁵ | 0033 283 ⁵⁸⁵ | 0.165 | 0124 535 ¹⁵⁴⁰ | 0627 ⁸ | 0069 005 ⁸⁵¹ |
| .116 | 0061 041 ¹⁰⁶⁶ | 0306 ⁵ | 0033 868 ⁵⁹¹ | .166 | 0126 075 ¹⁵⁴⁹ | 0635 ⁷ | 0069 856 ⁸⁵⁶ |
| .117 | 0062 107 ¹⁰⁷⁵ | 0312 ⁵ | 0034 459 ⁵⁹⁵ | .167 | 0127 624 ¹⁵⁶⁰ | 0642 ⁸ | 0070 712 ⁸⁶² |
| .118 | 0063 182 ¹⁰⁸⁵ | 0317 ⁵ | 0035 054 ⁶⁰¹ | .168 | 0129 184 ¹⁵⁶⁹ | 0650 ⁸ | 0071 574 ⁸⁶⁷ |
| .119 | 0064 267 ¹⁰⁹⁴ | 0322 ⁶ | 0035 655 ⁶⁰⁷ | .169 | 0130 753 ¹⁵⁷⁹ | 0658 ⁸ | 0072 441 ⁸⁷² |
| 0.120 | 0065 361 ¹¹⁰³ | 0328 ⁶ | 0036 262 ⁶¹¹ | 0.170 | 0132 332 ¹⁵⁸⁹ | 0666 ⁸ | 0073 313 ⁸⁷⁸ |
| .121 | 0066 464 ¹¹¹³ | 0334 ⁵ | 0036 873 ⁶¹⁷ | .171 | 0133 921 ¹⁶⁰⁰ | 0674 ⁸ | 0074 191 ⁸⁸⁴ |
| .122 | 0067 577 ¹¹²³ | 0339 ⁵ | 0037 490 ⁶²¹ | .172 | 0135 521 ¹⁶⁰⁹ | 0682 ⁸ | 0075 075 ⁸⁸⁹ |
| .123 | 0068 700 ¹¹³² | 0345 ⁵ | 0038 111 ⁶²⁷ | .173 | 0137 130 ¹⁶¹⁹ | 0691 ⁹ | 0075 964 ⁸⁹⁴ |
| .124 | 0069 832 ¹¹⁴¹ | 0350 ⁶ | 0038 738 ⁶³³ | .174 | 0138 749 ¹⁶²⁹ | 0699 ⁸ | 0076 858 ⁹⁰⁰ |
| 0.125 | 0070 973 ¹¹⁵² | 0356 ⁶ | 0039 371 ⁶³⁷ | 0.175 | 0140 378 ¹⁶⁴⁰ | 0707 ⁸ | 0077 758 ⁹⁰⁵ |
| .126 | 0072 125 ¹¹⁶⁰ | 0362 ⁶ | 0040 008 ⁶⁴³ | .176 | 0142 018 ¹⁶⁴⁹ | 0715 ⁹ | 0078 663 ⁹¹¹ |
| .127 | 0073 285 ¹¹⁷⁰ | 0368 ⁶ | 0040 651 ⁶⁴⁸ | .177 | 0143 667 ¹⁶⁵⁹ | 0724 ⁸ | 0079 574 ⁹¹⁶ |
| .128 | 0074 455 ¹¹⁸⁰ | 0374 ⁶ | 0041 299 ⁶⁵³ | .178 | 0145 326 ¹⁶⁷⁰ | 0732 ⁹ | 0080 490 ⁹²² |
| .129 | 0075 635 ¹¹⁸⁹ | 0380 ⁶ | 0041 952 ⁶⁵⁹ | .179 | 0146 996 ¹⁶⁷⁹ | 0741 ⁸ | 0081 412 ⁹²⁷ |
| 0.130 | 0076 824 ¹¹⁹⁹ | 0386 ⁶ | 0042 611 ⁶⁶⁴ | 0.180 | 0148 675 ¹⁶⁹⁰ | 0749 ⁹ | 0082 339 ⁹³³ |
| .131 | 0078 023 ¹²⁰⁸ | 0392 ⁶ | 0043 275 ⁶⁶⁹ | .181 | 0150 365 ¹⁷⁰⁰ | 0758 ⁸ | 0083 272 ⁹³⁹ |
| .132 | 0079 231 ¹²¹⁸ | 0398 ⁶ | 0043 944 ⁶⁷⁴ | .182 | 0152 065 ¹⁷¹⁰ | 0766 ⁹ | 0084 211 ⁹⁴³ |
| .133 | 0080 449 ¹²²⁷ | 0404 ⁶ | 0044 618 ⁶⁸⁰ | .183 | 0153 775 ¹⁷²⁰ | 0775 ⁹ | 0085 154 ⁹⁵⁰ |
| .134 | 0081 676 ¹²³⁷ | 0410 ⁶ | 0045 298 ⁶⁸⁴ | .184 | 0155 495 ¹⁷³⁰ | 0784 ⁹ | 0086 104 ⁹⁵⁵ |
| 0.135 | 0082 913 ¹²⁴⁷ | 0416 ⁷ | 0045 982 ⁶⁹¹ | 0.185 | 0157 225 ¹⁷⁴⁰ | 0793 ⁹ | 0087 059 ⁹⁶⁰ |
| .136 | 0084 160 ¹²⁵⁶ | 0423 ⁷ | 0046 673 ⁶⁹⁵ | .186 | 0158 965 ¹⁷⁵¹ | 0802 ⁹ | 0088 019 ⁹⁶⁶ |
| .137 | 0085 416 ¹²⁶⁶ | 0429 ⁶ | 0047 368 ⁷⁰¹ | .187 | 0160 716 ¹⁷⁶¹ | 0810 ⁹ | 0088 985 ⁹⁷² |
| .138 | 0086 682 ¹²⁷⁶ | 0435 ⁷ | 0048 069 ⁷⁰⁶ | .188 | 0162 477 ¹⁷⁷¹ | 0819 ⁹ | 0089 957 ⁹⁷⁷ |
| .139 | 0087 958 ¹²⁸⁵ | 0442 ⁶ | 0048 775 ⁷¹¹ | .189 | 0164 248 ¹⁷⁸¹ | 0828 ⁹ | 0090 934 ⁹⁸³ |
| 0.140 | 0089 243 ¹²⁹⁵ | 0448 ⁷ | 0049 486 ⁷¹⁷ | 0.190 | 0166 029 ¹⁷⁹¹ | 0837 ¹⁰ | 0091 917 ⁹⁸⁸ |
| .141 | 0090 538 ¹³⁰⁴ | 0455 ⁷ | 0050 203 ⁷²² | .191 | 0167 820 ¹⁸⁰² | 0847 ⁹ | 0092 905 ⁹⁹⁴ |
| .142 | 0091 842 ¹³¹⁴ | 0461 ⁷ | 0050 925 ⁷²⁷ | .192 | 0169 622 ¹⁸¹² | 0856 ⁹ | 0093 899 ⁹⁹⁹ |
| .143 | 0093 156 ¹³²⁴ | 0468 ⁷ | 0051 652 ⁷³³ | .193 | 0171 434 ¹⁸²² | 0865 ⁹ | 0094 898 ¹⁰⁰⁵ |
| .144 | 0094 480 ¹³³⁴ | 0475 ⁷ | 0052 385 ⁷³⁷ | .194 | 0173 256 ¹⁸³³ | 0874 ¹⁰ | 0095 903 ¹⁰¹¹ |
| 0.145 | 0095 814 ¹³⁴³ | 0482 ⁷ | 0053 122 ⁷⁴⁴ | 0.195 | 0175 089 ¹⁸⁴² | 0884 ⁹ | 0096 914 ¹⁰¹⁶ |
| .146 | 0097 157 ¹³⁵³ | 0488 ⁷ | 0053 866 ⁷⁴⁸ | .196 | 0176 931 ¹⁸⁵³ | 0893 ⁹ | 0097 930 ¹⁰²² |
| .147 | 0098 510 ¹³⁶³ | 0495 ⁷ | 0054 614 ⁷⁵⁴ | .197 | 0178 784 ¹⁸⁶⁴ | 0902 ⁹ | 0098 952 ¹⁰²⁸ |
| .148 | 0099 873 ¹³⁷² | 0502 ⁷ | 0055 368 ⁷⁵⁹ | .198 | 0180 648 ¹⁸⁷⁴ | 0912 ¹⁰ | 0099 980 ¹⁰³³ |
| .149 | 0101 245 ¹³⁸² | 0509 ⁷ | 0056 127 ⁷⁶⁵ | .199 | 0182 522 ¹⁸⁸⁴ | 0921 ¹⁰ | 0101 018 ¹⁰³⁸ |
| 0.150 | 0102 627 | 0516 | 0056 892 | 0.200 | 0184 406 | 0931 | 0102 051 |

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|--------------------------|--------------------|--------------------------|-----------------------------|--------------------------|--------------------|--------------------------|
| 1. | | 3. | 1. | 1. | | 3. | 1. |
| 0.200 | 0184 406 ¹⁸⁹⁴ | 0931 ¹⁰ | 0102 051 ¹⁰⁴⁵ | 0.250 | 0292 180 ²⁴³⁴ | 1484 ¹² | 0161 332 ¹³³⁶ |
| .201 | 0186 300 ¹⁹⁰⁵ | 0941 ⁹ | 0103 096 ¹⁰⁵⁰ | .251 | 0294 614 ²⁴⁴⁶ | 1496 ¹³ | 0162 668 ¹³⁴² |
| .202 | 0188 205 ¹⁹¹⁶ | 0950 ¹⁰ | 0104 146 ¹⁰⁵⁸ | .252 | 0297 060 ²⁴⁵⁷ | 1509 ¹³ | 0164 016 ¹³⁴⁸ |
| .203 | 0190 121 ¹⁹²⁶ | 0960 ¹⁰ | 0105 202 ¹⁰⁶¹ | .253 | 0299 517 ²⁴⁶⁸ | 1522 ¹² | 0165 358 ¹³⁵⁵ |
| .204 | 0192 047 ¹⁹³⁶ | 0970 ¹⁰ | 0106 263 ¹⁰⁶⁷ | .254 | 0301 985 ²⁴⁸⁰ | 1534 ¹³ | 0166 713 ¹³⁶⁰ |
| 0.205 | 0193 983 ¹⁹⁴⁶ | 0980 ¹⁰ | 0107 330 ¹⁰⁷³ | 0.255 | 0304 465 ²⁴⁹¹ | 1547 ¹³ | 0168 073 ¹³⁶⁶ |
| .206 | 0195 929 ¹⁹⁵⁸ | 0990 ¹⁰ | 0108 403 ¹⁰⁷⁸ | .256 | 0306 956 ²⁵⁰² | 1560 ¹³ | 0169 439 ¹³⁷³ |
| .207 | 0197 887 ¹⁹⁶⁷ | 1000 ¹⁰ | 0109 481 ¹⁰⁸⁴ | .257 | 0309 458 ²⁵¹⁴ | 1573 ¹³ | 0170 812 ¹³⁷⁸ |
| .208 | 0199 854 ¹⁹⁷⁸ | 1010 ¹⁰ | 0110 565 ¹⁰⁹⁰ | .258 | 0311 972 ²⁵²⁵ | 1586 ¹³ | 0172 190 ¹³⁸⁵ |
| .209 | 0201 832 ¹⁹⁸⁹ | 1020 ¹⁰ | 0111 655 ¹⁰⁹⁵ | .259 | 0314 497 ²⁵³⁶ | 1599 ¹³ | 0173 575 ¹³⁹¹ |
| 0.210 | 0203 821 ¹⁹⁹⁹ | 1030 ¹⁰ | 0112 750 ¹¹⁰¹ | 0.260 | 0317 033 ²⁵⁴⁸ | 1612 ¹³ | 0174 966 ¹³⁹⁶ |
| .211 | 0205 820 ²⁰¹⁰ | 1040 ¹¹ | 0113 851 ¹¹⁰⁷ | .261 | 0319 581 ²⁵⁶⁰ | 1625 ¹³ | 0176 362 ¹⁴⁰⁴ |
| .212 | 0207 830 ²⁰²⁰ | 1051 ¹¹ | 0114 958 ¹¹¹³ | .262 | 0322 141 ²⁵⁷⁰ | 1638 ¹³ | 0177 766 ¹⁴⁰⁹ |
| .213 | 0209 850 ²⁰³¹ | 1061 ¹⁰ | 0116 071 ¹¹¹⁸ | .263 | 0324 711 ²⁵⁸³ | 1652 ¹³ | 0179 175 ¹⁴¹⁵ |
| .214 | 0211 881 ²⁰⁴¹ | 1071 ¹¹ | 0117 189 ¹¹²⁴ | .264 | 0327 294 ²⁵⁹⁴ | 1665 ¹⁴ | 0180 590 ¹⁴²² |
| 0.215 | 0213 922 ²⁰⁵² | 1082 ¹⁰ | 0118 313 ¹¹³⁰ | 0.265 | 0329 888 ²⁶⁰⁵ | 1679 ¹³ | 0182 012 ¹⁴²⁷ |
| .216 | 0215 974 ²⁰⁶³ | 1092 ¹¹ | 0119 443 ¹¹³⁶ | .266 | 0332 493 ²⁶¹⁷ | 1692 ¹⁴ | 0183 439 ¹⁴³⁴ |
| .217 | 0218 037 ²⁰⁷³ | 1103 ¹⁰ | 0120 579 ¹¹⁴¹ | .267 | 0335 110 ²⁶²⁹ | 1706 ¹³ | 0184 873 ¹⁴⁴⁰ |
| .218 | 0220 116 ²⁰⁸⁴ | 1113 ¹⁰ | 0121 720 ¹¹⁴⁷ | .268 | 0337 739 ²⁶⁴⁰ | 1719 ¹³ | 0186 313 ¹⁴⁴⁷ |
| .219 | 0222 194 ²⁰⁹⁵ | 1124 ¹¹ | 0122 867 ¹¹⁵³ | .269 | 0340 379 ²⁶⁵² | 1733 ¹⁴ | 0187 760 ¹⁴⁵² |
| 0.220 | 0224 289 ²¹⁰⁵ | 1135 ¹¹ | 0124 020 ¹¹⁵⁹ | 0.270 | 0343 031 ²⁶⁶⁴ | 1747 ¹⁴ | 0189 212 ¹⁴⁵⁹ |
| .221 | 0226 394 ²¹¹⁶ | 1146 ¹⁰ | 0125 179 ¹¹⁶⁴ | .271 | 0345 695 ²⁶⁷⁵ | 1761 ¹³ | 0190 671 ¹⁴⁶⁵ |
| .222 | 0228 510 ²¹²⁷ | 1156 ¹¹ | 0126 343 ¹¹⁷⁰ | .272 | 0348 370 ²⁶⁸⁷ | 1774 ¹³ | 0192 136 ¹⁴⁷¹ |
| .223 | 0230 637 ²¹³⁸ | 1167 ¹¹ | 0127 513 ¹¹⁷⁶ | .273 | 0351 057 ²⁶⁹⁹ | 1788 ¹⁴ | 0193 607 ¹⁴⁷⁸ |
| .224 | 0232 775 ²¹⁴⁸ | 1178 ¹¹ | 0128 689 ¹¹⁸² | .274 | 0353 756 ²⁷¹¹ | 1802 ¹⁴ | 0195 085 ¹⁴⁸³ |
| 0.225 | 0234 923 ²¹⁵⁹ | 1189 ¹¹ | 0129 871 ¹¹⁸⁸ | 0.275 | 0356 467 ²⁷²² | 1816 ¹⁵ | 0196 568 ¹⁴⁹⁰ |
| .226 | 0237 082 ²¹⁷⁰ | 1200 ¹² | 0131 059 ¹¹⁹³ | .276 | 0359 189 ²⁷³⁴ | 1831 ¹⁴ | 0198 058 ¹⁴⁹⁷ |
| .227 | 0239 252 ²¹⁸¹ | 1212 ¹¹ | 0132 252 ¹²⁰⁰ | .277 | 0361 923 ²⁷⁴⁶ | 1845 ¹⁴ | 0199 555 ¹⁵⁰² |
| .228 | 0241 433 ²¹⁹¹ | 1223 ¹¹ | 0133 452 ¹²⁰⁵ | .278 | 0364 669 ²⁷⁵⁸ | 1859 ¹⁴ | 0201 057 ¹⁵⁰⁹ |
| .229 | 0243 624 ²²⁰³ | 1234 ¹¹ | 0134 657 ¹²¹¹ | .279 | 0367 427 ²⁷⁶⁹ | 1873 ¹⁵ | 0202 566 ¹⁵¹⁶ |
| 0.230 | 0245 827 ²²¹³ | 1245 ¹² | 0135 868 ¹²¹⁷ | 0.280 | 0370 196 ²⁷⁸² | 1888 ¹⁴ | 0204 082 ¹⁵²¹ |
| .231 | 0248 040 ²²²⁴ | 1257 ¹¹ | 0137 085 ¹²²³ | .281 | 0372 978 ²⁷⁹³ | 1902 ¹⁵ | 0205 603 ¹⁵²⁸ |
| .232 | 0250 264 ²²³⁵ | 1268 ¹⁰ | 0138 308 ¹²²⁹ | .282 | 0375 771 ²⁸⁰⁶ | 1917 ¹⁴ | 0207 131 ¹⁵³⁵ |
| .233 | 0252 496 ²²⁴⁶ | 1280 ¹¹ | 0139 537 ¹²³⁴ | .283 | 0378 577 ²⁸¹⁷ | 1931 ¹⁵ | 0208 666 ¹⁵⁴⁰ |
| .234 | 0254 745 ²²⁵⁷ | 1291 ¹² | 0140 771 ¹²⁴¹ | .284 | 0381 394 ²⁸³⁰ | 1946 ¹⁵ | 0210 206 ¹⁵⁴⁷ |
| 0.235 | 0257 002 ²²⁶⁸ | 1303 ¹¹ | 0142 012 ¹²⁴⁶ | 0.285 | 0384 224 ²⁸⁴¹ | 1961 ¹⁵ | 0211 753 ¹⁵⁵⁴ |
| .236 | 0259 270 ²²⁷⁸ | 1314 ¹² | 0143 258 ¹²⁵² | .286 | 0387 065 ²⁸⁵³ | 1976 ¹⁴ | 0213 307 ¹⁵⁶⁰ |
| .237 | 0261 548 ²²⁹⁰ | 1326 ¹² | 0144 510 ¹²⁵⁹ | .287 | 0389 918 ²⁸⁶⁶ | 1990 ¹⁵ | 0214 867 ¹⁵⁶⁶ |
| .238 | 0263 836 ²³⁰¹ | 1338 ¹² | 0145 769 ¹²⁶⁴ | .288 | 0392 784 ²⁸⁷⁸ | 2005 ¹⁵ | 0216 433 ¹⁵⁷³ |
| .239 | 0266 139 ²³¹² | 1350 ¹² | 0147 033 ¹²⁷⁰ | .289 | 0395 662 ²⁸⁸⁹ | 2020 ¹⁵ | 0218 006 ¹⁵⁷⁹ |
| 0.240 | 0268 451 ²³²³ | 1362 ¹¹ | 0148 303 ¹²⁷⁶ | 0.290 | 0398 551 ²⁹⁰² | 2035 ¹⁶ | 0219 585 ¹⁵⁸⁶ |
| .241 | 0270 774 ²³³⁴ | 1373 ¹² | 0149 579 ¹²⁸² | .291 | 0401 453 ²⁹¹⁴ | 2051 ¹⁵ | 0221 171 ¹⁵⁹² |
| .242 | 0273 108 ²³⁴⁵ | 1385 ¹³ | 0150 861 ¹²⁸⁸ | .292 | 0404 367 ²⁹²⁶ | 2066 ¹⁵ | 0222 763 ¹⁵⁹⁸ |
| .243 | 0275 453 ²³⁵⁶ | 1398 ¹² | 0152 149 ¹²⁹⁴ | .293 | 0407 293 ²⁹³⁹ | 2081 ¹⁵ | 0224 361 ¹⁶⁰⁵ |
| .244 | 0277 809 ²³⁶⁷ | 1410 ¹² | 0153 443 ¹³⁰⁰ | .294 | 0410 232 ²⁹⁵⁰ | 2096 ¹⁶ | 0225 966 ¹⁶¹² |
| 0.245 | 0280 176 ²³⁷⁸ | 1422 ¹² | 0154 743 ¹³⁰⁶ | 0.295 | 0413 182 ²⁹⁶³ | 2112 ¹⁵ | 0227 578 ¹⁶¹⁸ |
| .246 | 0282 554 ²³⁹⁰ | 1434 ¹² | 0156 049 ¹³¹¹ | .296 | 0416 145 ²⁹⁷⁵ | 2127 ¹⁶ | 0229 196 ¹⁶²⁴ |
| .247 | 0284 944 ²⁴⁰¹ | 1446 ¹³ | 0157 360 ¹³¹⁸ | .297 | 0419 120 ²⁹⁸⁸ | 2143 ¹⁵ | 0230 820 ¹⁶³¹ |
| .248 | 0287 345 ²⁴¹² | 1459 ¹² | 0158 678 ¹³²⁴ | .298 | 0422 108 ³⁰⁰⁰ | 2158 ¹⁶ | 0232 451 ¹⁶³⁸ |
| .249 | 0289 757 ²⁴²³ | 1471 ¹³ | 0160 002 ¹³³⁰ | .299 | 0425 108 ³⁰¹² | 2174 ¹⁶ | 0234 089 ¹⁶⁴⁴ |
| 0.250 | 0292 180 | 1484 | 0161 332 | 0.300 | 0428 120 | 2190 | 0235 733 |

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|--------------------------|--------------------|--------------------------|-----------------------------|--------------------------|--------------------|--------------------------|
| 1. | | 3. | 1. | 1. | | 3. | 1. |
| 0.300 | 0428 120 | 2190 ¹⁶ | 0235 733 | 0.350 | 0595 130 | 3072 ¹⁹ | 0326 580 |
| .301 | 0431 145 ³⁰²⁵ | 2206 ¹⁶ | 0237 384 ¹⁶⁵¹ | .351 | 0598 812 ³⁶⁸² | 3091 ²⁰ | 0328 575 ¹⁹⁹⁵ |
| .302 | 0434 182 ³⁰³⁷ | 2222 ¹⁶ | 0239 041 ¹⁶⁵⁷ | .352 | 0602 508 ³⁶⁹⁶ | 3111 ²⁰ | 0330 579 ²⁰⁰⁴ |
| .303 | 0437 231 ³⁰⁴⁹ | 2238 ¹⁶ | 0240 705 ¹⁶⁶⁴ | .353 | 0606 217 ³⁷⁰⁹ | 3131 ²⁰ | 0332 589 ²⁰¹⁰ |
| .304 | 0440 293 ³⁰⁶² | 2254 ¹⁶ | 0242 375 ¹⁶⁷⁰ | .354 | 0609 941 ³⁷²⁴ | 3150 ¹⁹ | 0334 607 ²⁰¹⁸ |
| | | | | | | | |
| 0.305 | 0443 368 ³⁰⁷⁵ | 2270 ¹⁶ | 0244 053 ¹⁶⁷⁸ | 0.355 | 0613 679 | 3170 ²⁰ | 0336 632 ²⁰²⁵ |
| .306 | 0446 455 ³⁰⁸⁷ | 2286 ¹⁶ | 0245 736 ¹⁶⁸³ | .356 | 0617 430 ³⁷⁵¹ | 3190 ²⁰ | 0338 664 ²⁰³² |
| .307 | 0449 554 ³⁰⁹⁹ | 2302 ¹⁶ | 0247 427 ¹⁶⁹¹ | .357 | 0621 196 ³⁷⁶⁶ | 3211 ²¹ | 0340 704 ²⁰⁴⁰ |
| .308 | 0452 667 ³¹¹³ | 2318 ¹⁶ | 0249 124 ¹⁶⁹⁷ | .358 | 0624 976 ³⁷⁸⁰ | 3231 ²⁰ | 0342 751 ²⁰⁴⁷ |
| .309 | 0455 791 ³¹²⁴ | 2335 ¹⁷ | 0250 827 ¹⁷⁰³ | .359 | 0628 770 ³⁷⁹⁴ | 3251 ²⁰ | 0344 805 ²⁰⁵⁴ |
| | | | | | | | |
| 0.310 | 0458 929 ³¹³⁸ | 2351 ¹⁷ | 0252 538 ¹⁷¹¹ | 0.360 | 0632 579 | 3271 ²⁰ | 0346 867 ²⁰⁶² |
| .311 | 0462 079 ³¹⁵⁰ | 2368 ¹⁷ | 0254 255 ¹⁷¹⁷ | .361 | 0636 402 ³⁸²³ | 3292 ²¹ | 0348 936 ²⁰⁶⁹ |
| .312 | 0465 242 ³¹⁶³ | 2384 ¹⁶ | 0255 978 ¹⁷²³ | .362 | 0640 239 ³⁸³⁷ | 3312 ²⁰ | 0351 013 ²⁰⁷⁷ |
| .313 | 0468 417 ³¹⁷⁵ | 2401 ¹⁷ | 0257 709 ¹⁷³¹ | .363 | 0644 090 ³⁸⁵¹ | 3333 ²¹ | 0353 097 ²⁰⁸⁴ |
| .314 | 0471 605 ³¹⁸⁸ | 2418 ¹⁷ | 0259 446 ¹⁷³⁷ | .364 | 0647 956 ³⁸⁶⁶ | 3354 ²¹ | 0355 188 ²⁰⁹¹ |
| | | | | | | | |
| 0.315 | 0474 807 ³²⁰² | 2435 ¹⁷ | 0261 190 ¹⁷⁴⁴ | 0.365 | 0651 836 | 3374 ²⁰ | 0357 287 ²⁰⁹⁹ |
| .316 | 0478 020 ³²¹³ | 2452 ¹⁷ | 0262 941 ¹⁷⁵¹ | .366 | 0655 731 ³⁸⁹⁵ | 3395 ²¹ | 0359 394 ²¹⁰⁷ |
| .317 | 0481 247 ³²²⁷ | 2469 ¹⁷ | 0264 698 ¹⁷⁵⁷ | .367 | 0659 640 ³⁹⁰⁹ | 3416 ²¹ | 0361 508 ²¹¹⁴ |
| .318 | 0484 487 ³²⁴⁰ | 2486 ¹⁷ | 0266 462 ¹⁷⁶⁴ | .368 | 0663 564 ³⁹²⁴ | 3437 ²¹ | 0363 630 ²¹²² |
| .319 | 0487 739 ³²⁵² | 2503 ¹⁷ | 0268 233 ¹⁷⁷¹ | .369 | 0667 503 ³⁹³⁹ | 3458 ²¹ | 0365 759 ²¹²⁹ |
| | | | | | | | |
| 0.320 | 0491 005 ³²⁶⁶ | 2520 ¹⁷ | 0270 011 ¹⁷⁷⁸ | 0.370 | 0671 456 | 3480 ²¹ | 0367 896 ²¹³⁷ |
| .321 | 0494 283 ³²⁷⁸ | 2537 ¹⁷ | 0271 796 ¹⁷⁸⁵ | .371 | 0675 423 ³⁹⁶⁷ | 3501 ²¹ | 0369 986 ²¹⁴⁴ |
| .322 | 0497 574 ³²⁹¹ | 2555 ¹⁸ | 0273 587 ¹⁷⁹¹ | .372 | 0679 406 ³⁹⁸³ | 3522 ²¹ | 0370 040 ²¹⁵² |
| .323 | 0500 879 ³³⁰⁵ | 2572 ¹⁷ | 0275 386 ¹⁷⁹⁹ | .373 | 0683 403 ³⁹⁹⁷ | 3544 ²² | 0372 192 ²¹⁶⁰ |
| .324 | 0504 196 ³³¹⁷ | 2590 ¹⁸ | 0277 191 ¹⁸⁰⁵ | .374 | 0687 415 ⁴⁰¹² | 3565 ²¹ | 0374 352 ²¹⁶⁷ |
| | | | | | | | |
| 0.325 | 0507 527 ³³³¹ | 2607 ¹⁸ | 0279 003 ¹⁸¹² | 0.375 | 0691 441 ⁴⁰²⁶ | 3587 ²² | 0376 519 ²¹⁷⁵ |
| .326 | 0510 870 ³³⁴³ | 2625 ¹⁸ | 0280 822 ¹⁸¹⁹ | .376 | 0695 483 ⁴⁰⁴² | 3609 ²² | 0378 694 ²¹⁸² |
| .327 | 0514 227 ³³⁵⁷ | 2642 ¹⁷ | 0282 648 ¹⁸²⁶ | .377 | 0699 539 ⁴⁰⁵⁶ | 3631 ²² | 0380 876 ²¹⁸⁹ |
| .328 | 0517 597 ³³⁷⁰ | 2660 ¹⁸ | 0284 480 ¹⁸³² | .378 | 0703 610 ⁴⁰⁷¹ | 3653 ²² | 0383 066 ²¹⁹⁸ |
| .329 | 0520 980 ³³⁸³ | 2678 ¹⁸ | 0286 320 ¹⁸⁴⁰ | .379 | 0707 697 ⁴⁰⁸⁷ | 3675 ²² | 0385 264 ²²⁰⁶ |
| | | | | | | | |
| 0.330 | 0524 376 ³³⁹⁶ | 2696 ¹⁸ | 0288 167 ¹⁸⁴⁷ | 0.380 | 0711 798 | 3697 ²² | 0387 470 ²²¹³ |
| .331 | 0527 786 ³⁴¹⁰ | 2714 ¹⁸ | 0290 020 ¹⁸⁵³ | .381 | 0715 915 ⁴¹¹⁷ | 3719 ²² | 0389 683 ²²²² |
| .332 | 0531 209 ³⁴²³ | 2732 ¹⁸ | 0291 881 ¹⁸⁶¹ | .382 | 0720 046 ⁴¹³¹ | 3741 ²² | 0391 905 ²²²⁸ |
| .333 | 0534 645 ³⁴³⁶ | 2750 ¹⁸ | 0293 748 ¹⁸⁶⁷ | .383 | 0724 193 ⁴¹⁴⁷ | 3764 ²³ | 0394 133 ²²³⁷ |
| .334 | 0538 095 ³⁴⁵⁰ | 2769 ¹⁹ | 0295 623 ¹⁸⁷⁵ | .384 | 0728 355 ⁴¹⁶² | 3786 ²² | 0396 370 ²²⁴⁵ |
| | | | | | | | |
| 0.335 | 0541 557 ³⁴⁶² | 2787 ¹⁸ | 0297 505 ¹⁸⁸² | 0.385 | 0732 532 | 3809 ²² | 0398 615 ²²⁵² |
| .336 | 0545 034 ³⁴⁷⁷ | 2805 ¹⁸ | 0299 393 ¹⁸⁸⁸ | .386 | 0736 724 ⁴¹⁹² | 3831 ²² | 0400 867 ²²⁶¹ |
| .337 | 0548 524 ³⁴⁹⁰ | 2824 ¹⁹ | 0301 289 ¹⁸⁹⁶ | .387 | 0740 931 ⁴²⁰⁷ | 3854 ²³ | 0403 128 ²²⁶⁸ |
| .338 | 0552 027 ³⁵⁰³ | 2842 ¹⁸ | 0303 191 ¹⁹⁰² | .388 | 0745 154 ⁴²²³ | 3877 ²³ | 0405 396 ²²⁷⁶ |
| .339 | 0555 544 ³⁵¹⁷ | 2861 ¹⁹ | 0305 101 ¹⁹¹⁰ | .389 | 0749 393 ⁴²³⁹ | 3900 ²³ | 0407 672 ²²⁸⁴ |
| | | | | | | | |
| 0.340 | 0559 074 ³⁵³⁰ | 2880 ¹⁹ | 0307 018 ¹⁹¹⁷ | 0.390 | 0753 647 | 3923 ²³ | 0409 956 ²²⁹² |
| .341 | 0562 618 ³⁵⁴⁴ | 2899 ¹⁹ | 0308 942 ¹⁹²⁴ | .391 | 0757 916 ⁴²⁶⁹ | 3946 ²³ | 0412 248 ²³⁰⁰ |
| .342 | 0566 176 ³⁵⁵⁸ | 2918 ¹⁹ | 0310 873 ¹⁹³¹ | .392 | 0762 201 ⁴²⁸⁵ | 3969 ²³ | 0414 548 ²³⁰⁷ |
| .343 | 0569 747 ³⁵⁷¹ | 2937 ¹⁹ | 0312 811 ¹⁹³⁸ | .393 | 0766 501 ⁴³⁰⁰ | 3993 ²⁴ | 0416 855 ²³¹⁶ |
| .344 | 0573 332 ³⁵⁸⁵ | 2956 ¹⁹ | 0314 757 ¹⁹⁴⁶ | .394 | 0770 817 ⁴³¹⁶ | 4016 ²³ | 0419 171 ²³²⁴ |
| | | | | | | | |
| 0.345 | 0576 930 ³⁵⁹⁸ | 2975 ¹⁹ | 0316 709 ¹⁹⁵² | 0.395 | 0775 149 | 4040 ²³ | 0421 495 ²³³² |
| .346 | 0580 543 ³⁶¹³ | 2994 ¹⁹ | 0318 669 ¹⁹⁶⁰ | .396 | 0779 496 ⁴³⁴⁷ | 4063 ²³ | 0423 827 ²³⁴⁰ |
| .347 | 0584 169 ³⁶²⁶ | 3013 ¹⁹ | 0320 636 ¹⁹⁶⁷ | .397 | 0783 859 ⁴³⁶³ | 4087 ²⁴ | 0426 167 ²³⁴⁸ |
| .348 | 0587 809 ³⁶⁴⁰ | 3032 ²⁰ | 0322 610 ¹⁹⁷⁴ | .398 | 0788 238 ⁴³⁷⁹ | 4111 ²⁴ | 0428 515 ²³⁵⁶ |
| .349 | 0591 463 ³⁶⁵⁴ | 3052 ¹⁹ | 0324 591 ¹⁹⁸¹ | .399 | 0792 633 ⁴³⁹⁵ | 4135 ²⁴ | 0430 871 ²³⁶⁴ |
| | | | | | | | |
| 0.350 | 0595 130 | 3072 | 0326 580 | 0.400 | 0797 043 | 4159 | 0433 235 ²³⁷³ |

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|--------------------------|--------------------|--------------------------|-----------------------------|--------------------------|--------------------|--------------------------|
| | 1. | 3. | 1. | | 1. | 3. | 1. |
| 0.400 | 0797 043 | 4159 | 0435 608 | 0.450 | 1038 906 | 5492 | 0565 081 |
| .401 | 0801 470 ⁴⁴²⁷ | 4183 ²⁴ | 0437 988 ²³⁸⁰ | .451 | 1044 194 ⁵²⁸⁸ | 5521 ²⁹ | 0567 898 ²⁸¹⁷ |
| .402 | 0805 912 ⁴⁴⁴² | 4207 ²⁴ | 0440 377 ²³⁸⁹ | .452 | 1049 500 ⁵³⁰⁶ | 5551 ³⁰ | 0570 724 ²⁸²⁶ |
| .403 | 0810 371 ⁴⁴⁵⁹ | 4231 ²⁴ | 0442 774 ²³⁹⁷ | .453 | 1054 825 ⁵³²⁵ | 5581 ³⁰ | 0573 560 ²⁸³⁶ |
| .404 | 0814 845 ⁴⁴⁷⁴ | 4256 ²⁵ | 0445 179 ²⁴⁰⁵ | .454 | 1060 168 ⁵³⁴³ | 5611 ³⁰ | 0576 405 ²⁸⁴⁵ |
| | 4401 | 24 | 2413 | | 5362 | 30 | 2855 |
| 0.405 | 0819 336 | 4280 | 0447 592 | 0.455 | 1065 530 | 5641 | 0579 260 |
| .406 | 0823 843 ⁴⁵⁰⁷ | 4305 ²⁵ | 0450 014 ²⁴²² | .456 | 1070 912 ⁵³⁸² | 5671 ³⁰ | 0582 124 ²⁸⁶⁴ |
| .407 | 0828 366 ⁴⁵²³ | 4329 ²⁴ | 0452 444 ²⁴³⁰ | .457 | 1076 312 ⁵⁴⁰⁰ | 5701 ³⁰ | 0584 997 ²⁸⁷³ |
| .408 | 0832 905 ⁴⁵³⁹ | 4354 ²⁵ | 0454 882 ²⁴³⁸ | .458 | 1081 731 ⁵⁴¹⁹ | 5735 ³¹ | 0587 880 ²⁸⁸³ |
| .409 | 0837 461 ⁴⁵⁵⁶ | 4379 ²⁵ | 0457 328 ²⁴⁴⁶ | .459 | 1087 169 ⁵⁴³⁸ | 5762 ³⁰ | 0590 773 ²⁸⁹³ |
| | 4572 | 25 | 2455 | | 5458 | 31 | 2902 |
| 0.410 | 0842 033 | 4404 | 0459 783 | 0.460 | 1092 627 | 5793 | 0593 675 |
| .411 | 0846 621 ⁴⁵⁸⁸ | 4429 ²⁵ | 0462 246 ²⁴⁶³ | .461 | 1098 103 ⁵⁴⁷⁶ | 5823 ³⁰ | 0596 587 ²⁹¹² |
| .412 | 0851 226 ⁴⁶⁰⁵ | 4454 ²⁵ | 0464 718 ²⁴⁷² | .462 | 1103 599 ⁵⁴⁹⁶ | 5854 ³¹ | 0599 509 ²⁹²² |
| .413 | 0855 847 ⁴⁶²¹ | 4480 ²⁶ | 0467 198 ²⁴⁸⁰ | .463 | 1109 115 ⁵⁵¹⁶ | 5885 ³¹ | 0602 440 ²⁹³¹ |
| .414 | 0860 485 ⁴⁶³⁸ | 4505 ²⁵ | 0469 686 ²⁴⁸⁸ | .464 | 1114 649 ⁵⁵³⁴ | 5917 ³² | 0605 381 ²⁹⁴¹ |
| | 4654 | 25 | 2497 | | 5554 | 31 | 2950 |
| 0.415 | 0865 139 | 4530 | 0472 183 | 0.465 | 1120 203 | 5948 | 0608 331 |
| .416 | 0869 810 ⁴⁶⁷¹ | 4556 ²⁶ | 0474 689 ²⁵⁰⁶ | .466 | 1125 777 ⁵⁵⁷⁴ | 5976 ³¹ | 0611 291 ²⁹⁶⁰ |
| .417 | 0874 498 ⁴⁶⁸⁸ | 4582 ²⁶ | 0477 203 ²⁵¹⁴ | .467 | 1131 370 ⁵⁵⁹³ | 6011 ³² | 0614 262 ²⁹⁷¹ |
| .418 | 0879 203 ⁴⁷⁰⁵ | 4608 ²⁶ | 0479 725 ²⁵²² | .468 | 1136 983 ⁵⁶¹³ | 6045 ³¹ | 0617 241 ²⁹⁷⁹ |
| .419 | 0883 924 ⁴⁷²¹ | 4634 ²⁶ | 0482 256 ²⁵³¹ | .469 | 1142 616 ⁵⁶³³ | 6074 ³² | 0620 231 ²⁹⁹⁰ |
| | 4738 | 26 | 2539 | | 5652 | 32 | 3000 |
| 0.420 | 0888 662 | 4660 | 0484 795 | 0.470 | 1148 268 | 6106 | 0623 231 |
| .421 | 0893 417 ⁴⁷⁵⁵ | 4686 ²⁶ | 0487 344 ²⁵⁴⁹ | .471 | 1153 941 ⁵⁶⁷³ | 6136 ³² | 0626 240 ³⁰⁰⁹ |
| .422 | 0898 189 ⁴⁷⁷² | 4712 ²⁶ | 0489 900 ²⁵⁵⁶ | .472 | 1159 633 ⁵⁶⁹² | 6170 ³² | 0629 260 ³⁰²⁰ |
| .423 | 0902 978 ⁴⁷⁸⁹ | 4738 ²⁶ | 0492 466 ²⁵⁶⁶ | .473 | 1165 346 ⁵⁷¹³ | 6205 ³³ | 0632 285 ³⁰²⁹ |
| .424 | 0907 784 ⁴⁸⁰⁶ | 4765 ²⁷ | 0495 040 ²⁵⁷⁴ | .474 | 1171 078 ⁵⁷³² | 6235 ³³ | 0635 329 ³⁰⁴⁰ |
| | 4824 | 26 | 2582 | | 5753 | 33 | 3049 |
| 0.425 | 0912 608 | 4791 | 0497 622 | 0.475 | 1176 831 | 6268 | 0638 378 |
| .426 | 0917 448 ⁴⁸⁴⁰ | 4818 ²⁷ | 0500 214 ²⁵⁹² | .476 | 1182 604 ⁵⁷⁷³ | 6301 ³³ | 0641 438 ³⁰⁶⁰ |
| .427 | 0922 305 ⁴⁸⁵⁷ | 4845 ²⁷ | 0502 814 ²⁶⁰⁰ | .477 | 1188 397 ⁵⁷⁹³ | 6335 ³² | 0644 507 ³⁰⁶⁹ |
| .428 | 0927 180 ⁴⁸⁷⁵ | 4872 ²⁷ | 0505 423 ²⁶⁰⁹ | .478 | 1194 210 ⁵⁸¹³ | 6366 ³³ | 0647 587 ³⁰⁸⁰ |
| .429 | 0932 072 ⁴⁸⁹² | 4899 ²⁷ | 0508 040 ²⁶¹⁷ | .479 | 1200 044 ⁵⁸³⁴ | 6400 ³⁴ | 0650 677 ³⁰⁹⁰ |
| | 4910 | 27 | 2627 | | 5855 | 33 | 3100 |
| 0.430 | 0936 982 | 4926 | 0510 667 | 0.480 | 1205 899 | 6433 | 0653 777 |
| .431 | 0941 909 ⁴⁹²⁷ | 4953 ²⁷ | 0513 302 ²⁶³⁵ | .481 | 1211 774 ⁵⁸⁷⁵ | 6466 ³³ | 0656 887 ³¹¹⁰ |
| .432 | 0946 853 ⁴⁹⁴⁴ | 4980 ²⁷ | 0515 946 ²⁶⁴⁴ | .482 | 1217 669 ⁵⁸⁹⁵ | 6500 ³⁴ | 0659 887 ³¹²¹ |
| .433 | 0951 815 ⁴⁹⁶² | 5008 ²⁸ | 0518 599 ²⁶⁵³ | .483 | 1223 586 ⁵⁹¹⁷ | 6533 ³³ | 0660 008 ³¹³¹ |
| .434 | 0956 795 ⁴⁹⁸⁰ | 5035 ²⁷ | 0521 261 ²⁶⁶² | .484 | 1229 523 ⁵⁹³⁷ | 6567 ³⁴ | 0663 139 ³¹⁴¹ |
| | 4997 | 28 | 2671 | | 5958 | 34 | 3151 |
| 0.435 | 0961 792 | 5063 | 0523 932 | 0.485 | 1235 481 | 6601 | 0669 431 |
| .436 | 0966 807 ⁵⁰¹⁵ | 5091 ²⁸ | 0526 611 ²⁶⁷⁹ | .486 | 1241 460 ⁵⁹⁷⁹ | 6635 ³⁴ | 0672 593 ³¹⁶² |
| .437 | 0971 839 ⁵⁰³² | 5119 ²⁸ | 0529 300 ²⁶⁸⁹ | .487 | 1247 461 ⁶⁰⁰¹ | 6670 ³⁵ | 0675 765 ³¹⁷² |
| .438 | 0976 890 ⁵⁰⁵¹ | 5147 ²⁸ | 0531 998 ²⁶⁹⁸ | .488 | 1253 482 ⁶⁰²¹ | 6704 ³⁵ | 0678 948 ³¹⁸³ |
| .439 | 0981 958 ⁵⁰⁶⁸ | 5175 ²⁸ | 0534 704 ²⁷⁰⁶ | .489 | 1259 524 ⁶⁰⁴² | 6739 ³⁵ | 0682 141 ³¹⁹³ |
| | 5087 | 28 | 2716 | | 6064 | 34 | 3204 |
| 0.440 | 0987 045 | 5203 | 0537 420 | 0.490 | 1265 588 | 6773 | 0685 345 |
| .441 | 0992 149 ⁵¹⁰⁴ | 5231 ²⁸ | 0540 145 ²⁷²⁵ | .491 | 1271 673 ⁶⁰⁸⁵ | 6808 ³⁵ | 0688 559 ³²¹⁴ |
| .442 | 0997 271 ⁵¹²² | 5260 ²⁹ | 0542 879 ²⁷³⁴ | .492 | 1277 780 ⁶¹⁰⁷ | 6843 ³⁵ | 0691 784 ³²²⁵ |
| .443 | 1002 412 ⁵¹⁴¹ | 5288 ²⁸ | 0545 622 ²⁷⁴³ | .493 | 1283 908 ⁶¹²⁸ | 6878 ³⁵ | 0695 020 ³²³⁶ |
| .444 | 1007 576 ⁵¹⁵⁸ | 5317 ²⁹ | 0548 374 ²⁷⁵² | .494 | 1290 057 ⁶¹⁴⁹ | 6913 ³⁵ | 0698 266 ³²⁴⁶ |
| | 5177 | 29 | 2762 | | 6171 | 36 | 3256 |
| 0.445 | 1012 747 | 5346 | 0551 136 | 0.495 | 1296 228 | 6949 | 0701 522 |
| .446 | 1017 942 ⁵¹⁹⁵ | 5375 ²⁹ | 0553 906 ²⁷⁷⁰ | .496 | 1302 421 ⁶¹⁹³ | 6984 ³⁵ | 0704 790 ³²⁶⁸ |
| .447 | 1023 155 ⁵²¹³ | 5404 ²⁹ | 0556 686 ²⁷⁸⁰ | .497 | 1308 636 ⁶²¹⁵ | 7020 ³⁶ | 0708 088 ³²⁷⁸ |
| .448 | 1028 387 ⁵²³² | 5433 ²⁹ | 0559 475 ²⁷⁸⁹ | .498 | 1314 873 ⁶²³⁷ | 7056 ³⁶ | 0711 357 ³²⁸⁹ |
| .449 | 1033 638 ⁵²⁵¹ | 5462 ²⁹ | 0562 273 ²⁷⁹⁸ | .499 | 1321 132 ⁶²⁵⁹ | 7092 ³⁶ | 0714 657 ³³⁰⁰ |
| | 5268 | 30 | 2808 | | 6280 | 36 | 3311 |
| 0.450 | 1038 906 | 5492 | 0565 081 | 0.500 | 1327 412 | 7128 | 0717 968 |

TABLE 1.

| $\epsilon^{\frac{1}{2}}\mu$ | A | I | N | $\epsilon^{\frac{1}{2}}\mu$ | A | I | N |
|-----------------------------|--------------------------|--------------------|--------------------------|-----------------------------|--------------------------|--------------------|--------------------------|
| 1. | | 3. | 1. | 1. | | | 1. |
| 0.500 | 1327 412 | 7128 ³⁶ | 0717 968 ³³²¹ | 0.550 | 1671 551 | 3.9148 | 0898 205 ³⁹¹⁷ |
| .501 | 1333 715 ⁶³⁰³ | 7164 ³⁷ | 0721 289 ³³³³ | .551 | 1679 079 ⁷⁵²⁸ | 9193 ⁴⁵ | 0902 122 ³⁹³⁰ |
| .502 | 1340 040 ⁶³²⁵ | 7201 ³⁷ | 0724 622 ³³⁴³ | .552 | 1686 634 ⁷⁵⁵⁵ | 9238 ⁴⁵ | 0906 052 ³⁹⁴⁴ |
| .503 | 1346 388 ⁶³⁴⁸ | 7238 ³⁷ | 0727 965 ³³⁵⁵ | .553 | 1694 216 ⁷⁵⁸² | 9283 ⁴⁵ | 0909 996 ³⁹⁵⁷ |
| .504 | 1352 757 ⁶³⁶⁹ | 7274 ³⁶ | 0731 320 ³³⁶⁵ | .554 | 1701 825 ⁷⁶⁰⁹ | 9329 ⁴⁶ | 0913 953 ³⁹⁶⁹ |
| | | 6393 ³⁷ | | | | 7637 ⁴⁶ | |
| 0.505 | 1359 150 | 7311 ³⁷ | 0734 685 ³³⁷⁷ | 0.555 | 1709 462 ⁷⁶⁶⁵ | 3.9375 | 0917 922 ³⁹⁸⁴ |
| .506 | 1365 565 ⁶⁴¹⁵ | 7348 ³⁸ | 0738 062 ³³⁸⁸ | .556 | 1717 127 ⁷⁶⁹² | 9421 ⁴⁶ | 0921 906 ³⁹⁹⁶ |
| .507 | 1372 002 ⁶⁴³⁷ | 7386 ³⁸ | 0741 450 ³³⁹⁹ | .557 | 1724 819 ⁷⁷²¹ | 9467 ⁴⁶ | 0925 902 ⁴⁰¹⁰ |
| .508 | 1378 462 ⁶⁴⁶⁰ | 7423 ³⁸ | 0744 849 ³⁴¹⁰ | .558 | 1732 540 ⁷⁷⁴⁸ | 9513 ⁴⁷ | 0929 912 ⁴⁰²³ |
| .509 | 1384 945 ⁶⁴⁸³ | 7461 ³⁸ | 0748 259 ³⁴²¹ | .559 | 1740 238 ⁷⁷⁷⁶ | 9560 ⁴⁷ | 0933 935 ⁴⁰³⁶ |
| | | 6506 ³⁷ | | | | | |
| 0.510 | 1391 451 | 7498 ³⁸ | 0751 680 ³⁴³³ | 0.560 | 1748 064 ⁷⁸⁰⁴ | 3.9607 | 0937 971 ⁴⁰⁵¹ |
| .511 | 1397 980 ⁶⁵²⁹ | 7536 ³⁸ | 0755 113 ³⁴⁴⁴ | .561 | 1755 868 ⁷⁸³³ | 9654 ⁴⁷ | 0942 022 ⁴⁰⁶³ |
| .512 | 1404 532 ⁶⁵⁵² | 7574 ³⁸ | 0758 557 ³⁴⁵⁵ | .562 | 1763 701 ⁷⁸⁶¹ | 9701 ⁴⁷ | 0946 085 ⁴⁰⁷⁸ |
| .513 | 1411 108 ⁶⁵⁷⁶ | 7612 ³⁹ | 0762 012 ³⁴⁶⁶ | .563 | 1771 562 ⁷⁸⁹⁰ | 9749 ⁴⁷ | 0950 163 ⁴⁰⁹¹ |
| .514 | 1417 706 ⁶⁵⁹⁸ | 7651 ³⁹ | 0765 478 ³⁴⁷⁸ | .564 | 1779 452 ⁷⁹¹⁹ | 9796 ⁴⁸ | 0954 254 ⁴¹⁰⁴ |
| | | 6622 ³⁸ | | | | | |
| 0.515 | 1424 328 | 7689 ³⁹ | 0768 956 ³⁴⁹⁰ | 0.565 | 1787 371 | 3.9844 | 0958 358 ⁴¹¹⁹ |
| .516 | 1430 973 ⁶⁶⁴⁵ | 7728 ³⁹ | 0772 446 ³⁵⁰¹ | .566 | 1795 318 ⁷⁹⁴⁷ | 9892 ⁴⁸ | 0962 477 ⁴¹³² |
| .517 | 1437 642 ⁶⁶⁶⁹ | 7767 ³⁹ | 0775 947 ³⁵¹² | .567 | 1803 294 ⁷⁹⁷⁶ | 9941 ⁴⁹ | 0966 609 ⁴¹⁴⁶ |
| .518 | 1444 335 ⁶⁶⁹³ | 7806 ³⁹ | 0779 459 ³⁵²⁴ | .568 | 1811 300 ⁸⁰⁰⁶ | 3.9989 | 0970 755 ⁴¹⁶⁰ |
| .519 | 1451 051 ⁶⁷¹⁶ | 7845 ³⁹ | 0782 983 ³⁵³⁶ | .569 | 1819 334 ⁸⁰³⁴ | 4.0038 | 0974 915 ⁴¹⁷⁴ |
| | | 6740 ³⁹ | | | | 8064 ⁴⁹ | |
| 0.520 | 1457 791 | 7884 ⁴⁰ | 0786 519 ³⁵⁴⁸ | 0.570 | 1827 398 | 4.0087 | 0979 089 ⁴¹⁸⁹ |
| .521 | 1464 555 ⁶⁷⁶⁴ | 7924 ⁴⁰ | 0790 067 ³⁵⁵⁹ | .571 | 1835 491 ⁸⁰⁹³ | 0136 ⁴⁹ | 0983 278 ⁴²⁰² |
| .522 | 1471 343 ⁶⁷⁸⁸ | 7964 ⁴⁰ | 0793 626 ³⁵⁷¹ | .572 | 1843 618 ⁸¹²³ | 0186 ⁵⁰ | 0987 480 ⁴²¹⁶ |
| .523 | 1478 155 ⁶⁸¹² | 8003 ⁴⁰ | 0797 197 ³⁵⁸² | .573 | 1851 767 ⁸¹⁵³ | 0235 ⁴⁹ | 0991 696 ⁴²³¹ |
| .524 | 1484 991 ⁶⁸³⁶ | 8043 ⁴¹ | 0800 779 ³⁵⁹⁵ | .574 | 1859 950 ⁸¹⁸³ | 0285 ⁵⁰ | 0995 927 ⁴²⁴⁵ |
| | | 6860 ⁴¹ | | | | 8212 ⁵⁰ | |
| 0.525 | 1491 851 | 8084 ⁴⁰ | 0804 374 ³⁶⁰⁶ | 0.575 | 1868 162 | 4.0335 | 1000 172 ⁴²⁵⁹ |
| .526 | 1498 736 ⁶⁸⁸⁵ | 8124 ⁴⁰ | 0807 980 ³⁶¹⁸ | .576 | 1876 405 ⁸²⁴³ | 0386 ⁵¹ | 1004 431 ⁴²⁷⁴ |
| .527 | 1505 645 ⁶⁹⁰⁹ | 8165 ⁴¹ | 0811 598 ³⁶³⁰ | .577 | 1884 678 ⁸²⁷³ | 0436 ⁵⁰ | 1008 705 ⁴²⁸⁸ |
| .528 | 1512 579 ⁶⁹³⁴ | 8205 ⁴⁰ | 0815 228 ³⁶⁴² | .578 | 1892 981 ⁸³⁰³ | 0487 ⁵¹ | 1012 993 ⁴³⁰³ |
| .529 | 1519 538 ⁶⁹⁵⁹ | 8246 ⁴¹ | 0818 870 ³⁶⁵⁵ | .579 | 1901 315 ⁸³³⁴ | 0538 ⁵¹ | 1017 296 ⁴³¹⁷ |
| | | 6983 ⁴¹ | | | | 8365 ⁵¹ | |
| 0.530 | 1526 521 | 8287 ⁴² | 0822 525 ³⁶⁶⁶ | 0.580 | 1909 680 | 4.0589 | 1021 613 ⁴³³² |
| .531 | 1533 530 ⁷⁰⁰⁹ | 8329 ⁴² | 0826 191 ³⁶⁷⁸ | .581 | 1918 075 ⁸³⁹⁵ | 0641 ⁵² | 1025 945 ⁴³⁴⁶ |
| .532 | 1540 563 ⁷⁰³³ | 8370 ⁴² | 0829 869 ³⁶⁹¹ | .582 | 1926 502 ⁸⁴²⁷ | 0693 ⁵² | 1030 291 ⁴³⁶¹ |
| .533 | 1547 621 ⁷⁰⁵⁸ | 8412 ⁴² | 0833 560 ³⁷⁰³ | .583 | 1934 959 ⁸⁴⁵⁷ | 0745 ⁵² | 1034 652 ⁴³⁷⁶ |
| .534 | 1554 705 ⁷⁰⁸⁴ | 8453 ⁴¹ | 0837 263 ³⁷¹⁵ | .584 | 1943 448 ⁸⁴⁸⁹ | 0797 ⁵² | 1039 028 ⁴³⁹¹ |
| | | 7108 ⁴² | | | | 8520 ⁵² | |
| 0.535 | 1561 813 | 8495 ⁴³ | 0840 978 ³⁷²⁷ | 0.585 | 1951 968 | 4.0849 | 1043 419 ⁴⁴⁰⁶ |
| .536 | 1568 948 ⁷¹³⁵ | 8538 ⁴² | 0844 705 ³⁷⁴⁰ | .586 | 1960 520 ⁸⁵⁵² | 0902 ⁵³ | 1047 825 ⁴⁴²¹ |
| .537 | 1576 107 ⁷¹⁵⁹ | 8580 ⁴² | 0848 445 ³⁷⁵² | .587 | 1969 103 ⁸⁵⁸³ | 0955 ⁵³ | 1052 246 ⁴⁴³⁶ |
| .538 | 1583 293 ⁷¹⁸⁶ | 8629 ⁴² | 0852 197 ³⁷⁶⁴ | .588 | 1977 719 ⁸⁶¹⁶ | 1008 ⁵³ | 1056 682 ⁴⁴⁵¹ |
| .539 | 1590 503 ⁷²¹⁰ | 8665 ⁴³ | 0855 961 ³⁷⁷⁷ | .589 | 1986 366 ⁸⁶⁴⁷ | 1062 ⁵⁴ | 1061 133 ⁴⁴⁶⁶ |
| | | 7237 ⁴³ | | | | 8679 ⁵⁴ | |
| 0.540 | 1597 740 ⁷²⁶³ | 8708 ⁴³ | 0859 738 ³⁷⁹⁰ | 0.590 | 1995 045 | 4.1116 | 1065 599 ⁴⁴⁸² |
| .541 | 1605 003 ⁷²⁸⁹ | 8751 ⁴³ | 0863 528 ³⁸⁰² | .591 | 2003 757 ⁸⁷¹² | 1169 ⁵³ | 1070 081 ⁴⁴⁹⁷ |
| .542 | 1612 292 ⁷³¹⁴ | 8794 ⁴³ | 0867 330 ³⁸¹⁵ | .592 | 2012 501 ⁸⁷⁴⁴ | 1224 ⁵⁴ | 1074 578 ⁴⁵¹² |
| .543 | 1619 606 ⁷³⁴¹ | 8838 ⁴⁴ | 0871 145 ³⁸²⁷ | .593 | 2021 278 ⁸⁷⁷⁷ | 1278 ⁵⁵ | 1079 090 ⁴⁵²⁷ |
| .544 | 1626 947 ⁷³⁶⁸ | 8882 ⁴³ | 0874 972 ³⁸⁴⁰ | .594 | 2030 088 ⁸⁸¹⁰ | 1333 ⁵⁵ | 1083 617 ⁴⁵⁴³ |
| | | | | | | 8842 ⁵⁵ | |
| 0.545 | 1634 315 | 8925 ⁴⁴ | 0878 812 ³⁸⁵³ | 0.595 | 2038 930 | 4.1388 | 1088 160 ⁴⁵⁵⁹ |
| .546 | 1641 709 ⁷³⁹⁴ | 8969 ⁴⁴ | 0882 665 ³⁸⁶⁵ | .596 | 2047 806 ⁸⁸⁷⁶ | 1443 ⁵⁵ | 1092 719 ⁴⁵⁷⁵ |
| .547 | 1649 129 ⁷⁴²⁰ | 9014 ⁴⁵ | 0886 530 ³⁸⁷⁹ | .597 | 2056 714 ⁸⁹⁰⁸ | 1499 ⁵⁶ | 1097 294 ⁴⁵⁹⁰ |
| .548 | 1656 576 ⁷⁴⁴⁷ | 9058 ⁴⁴ | 0890 409 ³⁸⁹¹ | .598 | 2065 656 ⁸⁹⁴² | 1554 ⁵⁶ | 1101 884 ⁴⁶⁰⁵ |
| .549 | 1664 050 ⁷⁴⁷⁴ | 9103 ⁴⁵ | 0894 300 ³⁹⁰⁵ | .599 | 2074 632 ⁸⁹⁷⁶ | 1610 ⁵⁷ | 1106 489 ⁴⁶²² |
| | | 7501 ⁴⁵ | | | | 9009 ⁵⁷ | |
| 0.550 | 1671 551 | 9148 | 0898 205 | 0.600 | 2083 641 | 4.1667 | 1111 111 |

TABLE 2.

| ε | c | h | ε | c | h |
|---------------|----------------------------|-----------------------|---------------|---------------------------|-----------------------|
| 0.000 | 1.000 0000 | 0.00000 | 0.050 | 0.979 7508 | 0.05149 |
| .001 | 0.999 5999 ¹⁰⁰¹ | .00100 ¹⁰⁰ | .051 | .979 3406 ¹¹⁰² | .05256 ¹⁰⁷ |
| .002 | .999 1996 ¹⁰⁰³ | .00200 ¹⁰⁰ | .052 | .978 9302 ¹¹⁰⁴ | .05362 ¹⁰⁶ |
| .003 | .998 7991 ¹⁰⁰⁵ | .00301 ¹⁰¹ | .053 | .978 5196 ¹¹⁰⁶ | .05468 ¹⁰⁶ |
| .004 | .998 3984 ¹⁰⁰⁷ | .00401 ¹⁰⁰ | .054 | .978 1088 ¹¹⁰⁸ | .05575 ¹⁰⁷ |
| | 4008 | 100 | | 4111 | 106 |
| 0.005 | 0.997 9976 | 0.00501 | 0.055 | 0.977 6977 | 0.05681 |
| .006 | .997 5965 ¹⁰¹¹ | .00602 ¹⁰¹ | .056 | .977 2865 ¹¹¹² | .05788 ¹⁰⁷ |
| .007 | .997 1952 ¹⁰¹³ | .00703 ¹⁰¹ | .057 | .976 8750 ¹¹¹⁵ | .05895 ¹⁰⁷ |
| .008 | .996 7938 ¹⁰¹⁴ | .00804 ¹⁰¹ | .058 | .976 4633 ¹¹¹⁷ | .06002 ¹⁰⁷ |
| .009 | .996 3921 ¹⁰¹⁷ | .00905 ¹⁰¹ | .059 | .976 0514 ¹¹¹⁹ | .06109 ¹⁰⁷ |
| | 4019 | 101 | | 4121 | 108 |
| 0.010 | 0.995 9902 | 0.01006 | 0.060 | 0.975 6393 | 0.06217 |
| .011 | .995 5882 ¹⁰²⁰ | .01107 ¹⁰¹ | .061 | .975 2270 ¹¹²³ | .06324 ¹⁰⁷ |
| .012 | .995 1859 ¹⁰²³ | .01208 ¹⁰¹ | .062 | .974 8145 ¹¹²⁵ | .06432 ¹⁰⁸ |
| .013 | .994 7835 ¹⁰²⁴ | .01310 ¹⁰² | .063 | .974 4017 ¹¹²⁸ | .06539 ¹⁰⁷ |
| .014 | .994 3808 ¹⁰²⁷ | .01411 ¹⁰¹ | .064 | .973 9888 ¹¹²⁹ | .06647 ¹⁰⁸ |
| | 4028 | 102 | | 4132 | 108 |
| 0.015 | 0.993 9780 | 0.01513 | 0.065 | 0.973 5756 | 0.06755 |
| .016 | .993 5749 ¹⁰³¹ | .01615 ¹⁰² | .066 | .973 1622 ¹¹³⁴ | .06863 ¹⁰⁸ |
| .017 | .993 1717 ¹⁰³² | .01717 ¹⁰² | .067 | .972 7486 ¹¹³⁶ | .06971 ¹⁰⁸ |
| .018 | .992 7682 ¹⁰³⁵ | .01820 ¹⁰³ | .068 | .972 3348 ¹¹³⁸ | .07080 ¹⁰⁹ |
| .019 | .992 3646 ¹⁰³⁶ | .01921 ¹⁰¹ | .069 | .971 9207 ¹¹⁴¹ | .07188 ¹⁰⁸ |
| | 4039 | 102 | | 4142 | 109 |
| 0.020 | 0.991 9607 | 0.02023 | 0.070 | 0.971 5065 | 0.07297 |
| .021 | .991 5567 ¹⁰⁴⁰ | .02126 ¹⁰³ | .071 | .971 0920 ¹¹⁴⁵ | .07405 ¹⁰⁸ |
| .022 | .991 1525 ¹⁰⁴² | .02228 ¹⁰² | .072 | .970 6773 ¹¹⁴⁷ | .07514 ¹⁰⁹ |
| .023 | .990 7480 ¹⁰⁴⁵ | .02331 ¹⁰³ | .073 | .970 2624 ¹¹⁴⁹ | .07623 ¹⁰⁹ |
| .024 | .990 3434 ¹⁰⁴⁶ | .02434 ¹⁰³ | .074 | .969 8473 ¹¹⁵¹ | .07732 ¹⁰⁹ |
| | 4049 | 103 | | 4153 | 110 |
| 0.025 | 0.989 9385 | 0.02537 | 0.075 | 0.969 4320 | 0.07842 |
| .026 | .989 5335 ¹⁰⁵⁰ | .02640 ¹⁰³ | .076 | .969 0164 ¹¹⁵⁶ | .07951 ¹⁰⁹ |
| .027 | .989 1282 ¹⁰⁵³ | .02743 ¹⁰³ | .077 | .968 6006 ¹¹⁵⁸ | .08061 ¹¹⁰ |
| .028 | .988 7228 ¹⁰⁵⁴ | .02846 ¹⁰³ | .078 | .968 1846 ¹¹⁶⁰ | .08170 ¹⁰⁹ |
| .029 | .988 3171 ¹⁰⁵⁷ | .02950 ¹⁰⁴ | .079 | .967 7684 ¹¹⁶² | .08280 ¹¹⁰ |
| | 4059 | 103 | | 4164 | 110 |
| 0.030 | 0.987 9112 | 0.03053 | 0.080 | 0.967 3520 | 0.08390 |
| .031 | .987 5052 ¹⁰⁶⁰ | .03157 ¹⁰⁴ | .081 | .966 9353 ¹¹⁶⁷ | .08500 ¹¹⁰ |
| .032 | .987 0989 ¹⁰⁶³ | .03260 ¹⁰³ | .082 | .966 5184 ¹¹⁶⁹ | .08610 ¹¹⁰ |
| .033 | .986 6924 ¹⁰⁶⁵ | .03364 ¹⁰⁴ | .083 | .966 1013 ¹¹⁷¹ | .08721 ¹¹¹ |
| .034 | .986 2857 ¹⁰⁶⁷ | .03468 ¹⁰⁴ | .084 | .965 6840 ¹¹⁷³ | .08831 ¹¹⁰ |
| | 4068 | 104 | | 4175 | 111 |
| 0.035 | 0.985 8789 | 0.03572 | 0.085 | 0.965 2665 | 0.08942 |
| .036 | .985 4718 ¹⁰⁷¹ | .03677 ¹⁰⁵ | .086 | .964 8487 ¹¹⁷⁸ | .09052 ¹¹⁰ |
| .037 | .985 0645 ¹⁰⁷³ | .03781 ¹⁰⁴ | .087 | .964 4307 ¹¹⁸⁰ | .09163 ¹¹¹ |
| .038 | .984 6570 ¹⁰⁷⁵ | .03886 ¹⁰⁵ | .088 | .964 0125 ¹¹⁸² | .09274 ¹¹¹ |
| .039 | .984 2493 ¹⁰⁷⁷ | .03990 ¹⁰⁴ | .089 | .963 5941 ¹¹⁸⁴ | .09385 ¹¹¹ |
| | 4079 | 105 | | 4187 | 112 |
| 0.040 | 0.983 8414 | 0.04095 | 0.090 | 0.963 1754 | 0.09497 |
| .041 | .983 4333 ¹⁰⁸¹ | .04200 ¹⁰⁵ | .091 | .962 7566 ¹¹⁸⁸ | .09608 ¹¹¹ |
| .042 | .983 0249 ¹⁰⁸⁴ | .04305 ¹⁰⁵ | .092 | .962 3374 ¹¹⁹² | .09720 ¹¹² |
| .043 | .982 6164 ¹⁰⁸⁵ | .04410 ¹⁰⁵ | .093 | .961 9181 ¹¹⁹³ | .09831 ¹¹¹ |
| .044 | .982 2077 ¹⁰⁸⁷ | .04515 ¹⁰⁵ | .094 | .961 4986 ¹¹⁹⁵ | .09943 ¹¹² |
| | 4090 | 106 | | 4198 | 112 |
| 0.045 | 0.981 7987 | 0.04621 | 0.095 | 0.961 0788 | 0.10055 |
| .046 | .981 3896 ¹⁰⁹¹ | .04726 ¹⁰⁵ | .096 | .960 6588 ¹²⁰⁰ | .10167 ¹¹² |
| .047 | .980 9802 ¹⁰⁹⁴ | .04832 ¹⁰⁶ | .097 | .960 2385 ¹²⁰³ | .10279 ¹¹³ |
| .048 | .980 5706 ¹⁰⁹⁶ | .04937 ¹⁰⁵ | .098 | .959 8181 ¹²⁰⁴ | .10392 ¹¹² |
| .049 | .980 1608 ¹⁰⁹⁸ | .05043 ¹⁰⁶ | .099 | .959 3974 ¹²⁰⁷ | .10504 ¹¹² |
| | 4100 | 106 | | 4209 | 113 |
| 0.050 | 0.979 7508 | 0.05149 | 0.100 | 0.958 9765 | 0.10617 |

TABLE 3.

| $\varepsilon^{\frac{1}{2}}\sigma$ | J | K | $\varepsilon^{\frac{1}{2}}\sigma$ | J | K |
|-----------------------------------|---------------------------|-------------------------|-----------------------------------|---------------------------|-------------------------|
| 0.000 | 1.000 0000 | 0.000 0000 | 0.050 | 0.999 6250 ¹⁵¹ | 0.000 0071 ³ |
| .001 | 0.999 9998 ² | 0.000 0000 ⁰ | .051 | .999 6099 ¹⁵¹ | .0074 ³ |
| .002 | .999 9994 ⁴ | 0.000 0000 ⁰ | .052 | .999 5944 ¹⁵⁵ | .0077 ³ |
| .003 | .999 9986 ⁸ | 0.000 0000 ⁰ | .053 | .999 5787 ¹⁵⁷ | .0080 ³ |
| .004 | .999 9976 ¹⁰ | 0.000 0000 ⁰ | .054 | .999 5626 ¹⁶¹ | .0083 ³ |
| | | | | | |
| 0.005 | 0.999 9962 ¹⁴ | 0.000 0001 ⁰ | 0.055 | 0.999 5463 ¹⁶⁷ | 0.000 0086 ³ |
| .006 | .999 9946 ¹⁶ | 0.001 0001 ⁰ | .056 | .999 5296 ¹⁶⁹ | .0089 ³ |
| .007 | .999 9926 ²⁰ | 0.001 0001 ⁰ | .057 | .999 5127 ¹⁷³ | .0093 ⁴ |
| .008 | .999 9904 ²² | 0.002 0002 ¹ | .058 | .999 4954 ¹⁷⁵ | .0096 ³ |
| .009 | .999 9878 ²⁶ | 0.002 0002 ¹ | .059 | .999 4779 ¹⁷⁹ | .0099 ³ |
| | | | | | |
| 0.010 | 0.999 9850 ²⁸ | 0.000 0003 ⁰ | 0.060 | 0.999 4600 ¹⁸¹ | 0.000 0103 ³ |
| .011 | .999 9818 ³² | 0.003 0003 ⁰ | .061 | .999 4419 ¹⁸⁵ | .0106 ³ |
| .012 | .999 9784 ³⁴ | 0.004 0004 ¹ | .062 | .999 4234 ¹⁸⁷ | .0110 ⁴ |
| .013 | .999 9746 ³⁸ | 0.005 0005 ¹ | .063 | .999 4047 ¹⁹¹ | .0113 ³ |
| .014 | .999 9706 ⁴⁰ | 0.006 0006 ¹ | .064 | .999 3856 ¹⁹³ | .0117 ⁴ |
| | | | | | |
| 0.015 | 0.999 9662 ⁴⁴ | 0.000 0006 ¹ | 0.065 | 0.999 3663 ¹⁹⁷ | 0.000 0121 ³ |
| .016 | .999 9616 ⁴⁶ | 0.007 0007 ¹ | .066 | .999 3466 ¹⁹⁹ | .0124 ³ |
| .017 | .999 9566 ⁵⁰ | 0.008 0008 ¹ | .067 | .999 3267 ²⁰³ | .0128 ⁴ |
| .018 | .999 9514 ⁵² | 0.009 0009 ¹ | .068 | .999 3064 ²⁰⁵ | .0132 ⁴ |
| .019 | .999 9458 ⁵⁶ | 0.010 0010 ¹ | .069 | .999 2859 ²⁰⁹ | .0136 ⁴ |
| | | | | | |
| 0.020 | 0.999 9400 ⁵⁸ | 0.000 0011 ² | 0.070 | 0.999 2650 ²¹¹ | 0.000 0140 ⁴ |
| .021 | .999 9338 ⁶² | 0.013 0013 ² | .071 | .999 2439 ²¹⁵ | .0144 ⁴ |
| .022 | .999 9274 ⁶⁴ | 0.014 0014 ¹ | .072 | .999 2224 ²¹⁷ | .0148 ⁴ |
| .023 | .999 9206 ⁶⁸ | 0.015 0015 ¹ | .073 | .999 2007 ²²¹ | .0152 ⁴ |
| .024 | .999 9136 ⁷⁰ | 0.016 0016 ² | .074 | .999 1786 ²²³ | .0156 ⁴ |
| | | | | | |
| 0.025 | 0.999 9062 ⁷⁴ | 0.000 0018 ¹ | 0.075 | 0.999 1563 ²²⁷ | 0.000 0160 ⁵ |
| .026 | .999 8986 ⁷⁶ | 0.019 0019 ¹ | .076 | .999 1336 ²²⁹ | .0165 ⁵ |
| .027 | .999 8907 ⁷⁹ | 0.021 0021 ² | .077 | .999 1107 ²³³ | .0169 ⁴ |
| .028 | .999 8824 ⁸³ | 0.022 0022 ¹ | .078 | .999 0874 ²³⁵ | .0173 ⁵ |
| .029 | .999 8739 ⁸⁵ | 0.024 0024 ² | .079 | .999 0639 ²³⁹ | .0178 ⁵ |
| | | | | | |
| 0.030 | 0.999 8650 ⁸⁹ | 0.000 0026 ¹ | 0.080 | 0.999 0400 ²⁴¹ | 0.000 0182 ⁵ |
| .031 | .999 8559 ⁹¹ | 0.027 0027 ¹ | .081 | .999 0159 ²⁴⁵ | .0187 ⁵ |
| .032 | .999 8464 ⁹⁵ | 0.029 0029 ² | .082 | .998 9914 ²⁴⁵ | .0192 ⁵ |
| .033 | .999 8367 ⁹⁷ | 0.031 0031 ² | .083 | .998 9667 ²⁴⁷ | .0196 ⁵ |
| .034 | .999 8266 ¹⁰¹ | 0.033 0033 ² | .084 | .998 9416 ²⁵¹ | .0201 ⁵ |
| | | | | | |
| 0.035 | 0.999 8163 ¹⁰³ | 0.000 0035 ² | 0.085 | 0.998 9163 ²⁵³ | 0.000 0206 ⁵ |
| .036 | .999 8056 ¹⁰⁷ | 0.037 0037 ² | .086 | .998 8906 ²⁵⁷ | .0211 ⁵ |
| .037 | .999 7947 ¹⁰⁹ | 0.039 0039 ² | .087 | .998 8647 ²⁵⁹ | .0216 ⁵ |
| .038 | .999 7834 ¹¹³ | 0.041 0041 ² | .088 | .998 8384 ²⁶³ | .0221 ⁵ |
| .039 | .999 7719 ¹¹⁵ | 0.043 0043 ³ | .089 | .998 8119 ²⁶⁵ | .0226 ⁵ |
| | | | | | |
| 0.040 | 0.999 7600 ¹¹⁹ | 0.000 0046 ² | 0.090 | 0.998 7850 ²⁶⁹ | 0.000 0231 ⁵ |
| .041 | .999 7479 ¹²¹ | 0.048 0048 ² | .091 | .998 7579 ²⁷¹ | .0236 ⁵ |
| .042 | .999 7354 ¹²⁵ | 0.050 0050 ² | .092 | .998 7305 ²⁷⁴ | .0241 ⁵ |
| .043 | .999 7227 ¹²⁷ | 0.053 0053 ³ | .093 | .998 7027 ²⁷⁸ | .0246 ⁶ |
| .044 | .999 7096 ¹³¹ | 0.055 0055 ³ | .094 | .998 6747 ²⁸⁰ | .0252 ⁶ |
| | | | | | |
| 0.045 | 0.999 6963 ¹³³ | 0.000 0058 ² | 0.095 | 0.998 6463 ²⁸⁴ | 0.000 0257 ⁵ |
| .046 | .999 6826 ¹³⁷ | 0.060 0060 ² | .096 | .998 6177 ²⁸⁶ | .0262 ⁵ |
| .047 | .999 6687 ¹⁴³ | 0.063 0063 ³ | .097 | .998 5887 ²⁹⁰ | .0268 ⁶ |
| .048 | .999 6544 ¹⁴⁵ | 0.066 0066 ³ | .098 | .998 5595 ²⁹² | .0273 ⁶ |
| .049 | .999 6399 ¹⁴⁹ | 0.069 0069 ³ | .099 | .998 5299 ²⁹⁶ | .0279 ⁶ |
| | | | | | |
| 0.050 | 0.999 6250 | 0.000 0071 | 0.100 | 0.998 5001 | 0.000 0285 |

TABLE 3.

| $\epsilon^{\pm\sigma}$ | J | K | $\epsilon^{\pm\sigma}$ | J | K |
|------------------------|---------------------------|-------------------------|------------------------|---------------------------|--------------------------|
| 0.100 | 0.998 5001 ³⁰² | 0.000 0285 ⁵ | 0.150 | 0.996 6254 ⁴⁵² | 0.000 0637 ⁹ |
| .101 | .998 4699 ³⁰⁴ | 0290 ⁵ | .151 | .996 5802 ⁴⁵⁴ | 0646 ⁹ |
| .102 | .998 4395 ³⁰⁸ | 0296 ⁵ | .152 | .996 5348 ⁴⁵⁸ | 0654 ⁹ |
| .103 | .998 4087 ³¹⁰ | 0302 ⁵ | .153 | .996 4890 ⁴⁶⁰ | 0663 ⁹ |
| .104 | .998 3777 ³¹⁴ | 0308 ⁶ | .154 | .996 4430 ⁴⁶³ | 0671 ⁹ |
| 0.105 | 0.998 3463 ³¹⁶ | 0.000 0314 ⁵ | 0.155 | 0.996 3967 ⁴⁶⁷ | 0.000 0680 ⁹ |
| .106 | .998 3147 ³²⁰ | 0320 ⁵ | .156 | .996 3500 ⁴⁶⁹ | 0689 ⁹ |
| .107 | .998 2827 ³²² | 0326 ⁵ | .157 | .996 3031 ⁴⁷³ | 0697 ⁹ |
| .108 | .998 2505 ³²⁵ | 0332 ⁵ | .158 | .996 2558 ⁴⁷⁵ | 0706 ⁹ |
| .109 | .998 2186 ³²⁹ | 0338 ⁶ | .159 | .996 2083 ⁴⁷⁸ | 0715 ⁹ |
| 0.110 | 0.998 1851 ³³¹ | 0.000 0344 ⁶ | 0.160 | 0.996 1605 ⁴⁸² | 0.000 0724 ⁹ |
| .111 | .998 1520 ³³⁵ | 0350 ⁷ | .161 | .996 1123 ⁴⁸⁴ | 0733 ⁹ |
| .112 | .998 1185 ³³⁷ | 0357 ⁷ | .162 | .996 0639 ⁴⁸⁷ | 0742 ⁹ |
| .113 | .998 0848 ³⁴¹ | 0363 ⁸ | .163 | .996 0152 ⁴⁹¹ | 0751 ⁹ |
| .114 | .998 0507 ³⁴³ | 0369 ⁷ | .164 | .995 9661 ⁴⁹³ | 0760 ⁹ |
| 0.115 | 0.998 0164 ³⁴⁷ | 0.000 0376 ⁵ | 0.165 | 0.995 9168 ⁴⁹⁷ | 0.000 0769 ¹⁰ |
| .116 | .997 9817 ³⁴⁹ | 0382 ⁷ | .166 | .995 8671 ⁴⁹⁹ | 0779 ⁹ |
| .117 | .997 9468 ³⁵³ | 0389 ⁷ | .167 | .995 8172 ⁵⁰² | 0788 ⁹ |
| .118 | .997 9115 ³⁵⁵ | 0396 ⁷ | .168 | .995 7670 ⁵⁰⁶ | 0797 ¹⁰ |
| .119 | .997 8760 ³⁵⁹ | 0402 ⁷ | .169 | .995 7164 ⁵⁰⁸ | 0807 ⁹ |
| 0.120 | 0.997 8401 ³⁶¹ | 0.000 0409 ⁷ | 0.170 | 0.995 6656 ⁵¹¹ | 0.000 0816 ¹⁰ |
| .121 | .997 8040 ³⁶⁴ | 0416 ⁷ | .171 | .995 6145 ⁵¹⁵ | 0826 ¹⁰ |
| .122 | .997 7676 ³⁶⁸ | 0423 ⁷ | .172 | .995 5630 ⁵¹⁷ | 0835 ⁹ |
| .123 | .997 7308 ³⁷⁰ | 0430 ⁷ | .173 | .995 5113 ⁵²⁰ | 0845 ¹⁰ |
| .124 | .997 6938 ³⁷⁴ | 0437 ⁷ | .174 | .995 4593 ⁵²⁴ | 0855 ⁹ |
| 0.125 | 0.997 6564 ³⁷⁶ | 0.000 0444 ⁷ | 0.175 | 0.995 4069 ⁵²⁶ | 0.000 0864 ¹⁰ |
| .126 | .997 6188 ³⁸⁰ | 0451 ⁷ | .176 | .995 3543 ⁵²⁹ | 0874 ¹⁰ |
| .127 | .997 5808 ³⁸² | 0458 ⁷ | .177 | .995 3014 ⁵³³ | 0884 ¹⁰ |
| .128 | .997 5426 ³⁸⁶ | 0465 ⁷ | .178 | .995 2481 ⁵³⁵ | 0894 ¹⁰ |
| .129 | .997 5040 ³⁸⁸ | 0472 ⁸ | .179 | .995 1946 ⁵³⁸ | 0904 ¹⁰ |
| 0.130 | 0.997 4652 ³⁹¹ | 0.000 0480 ⁷ | 0.180 | 0.995 1408 ⁵⁴² | 0.000 0914 ¹⁰ |
| .131 | .997 4261 ³⁹⁵ | 0487 ⁷ | .181 | .995 0866 ⁵⁴⁴ | 0924 ¹⁰ |
| .132 | .997 3866 ³⁹⁷ | 0494 ⁷ | .182 | .995 0325 ⁵⁴⁷ | 0934 ¹⁰ |
| .133 | .997 3469 ⁴⁰¹ | 0502 ⁸ | .183 | .994 9775 ⁵⁵¹ | 0944 ¹⁰ |
| .134 | .997 3068 ⁴⁰³ | 0509 ⁸ | .184 | .994 9224 ⁵⁵³ | 0954 ¹¹ |
| 0.135 | 0.997 2665 ⁴⁰⁷ | 0.000 0517 ⁸ | 0.185 | 0.994 8671 ⁵⁵⁶ | 0.000 0965 ¹⁰ |
| .136 | .997 2258 ⁴⁰⁹ | 0525 ⁸ | .186 | .994 8115 ⁵⁶⁰ | 0975 ¹⁰ |
| .137 | .997 1849 ⁴¹² | 0532 ⁸ | .187 | .994 7553 ⁵⁶² | 0985 ¹¹ |
| .138 | .997 1437 ⁴¹⁶ | 0540 ⁸ | .188 | .994 6993 ⁵⁶⁵ | 0996 ¹⁰ |
| .139 | .997 1021 ⁴¹⁸ | 0548 ⁸ | .189 | .994 6428 ⁵⁶⁹ | 1006 ¹¹ |
| 0.140 | 0.997 0603 ⁴²² | 0.000 0556 ⁸ | 0.190 | 0.994 5859 ⁵⁷¹ | 0.000 1017 ¹⁰ |
| .141 | .997 0181 ⁴²⁴ | 0564 ⁸ | .191 | .994 5288 ⁵⁷⁴ | 1027 ¹¹ |
| .142 | .996 9757 ⁴²⁸ | 0572 ⁸ | .192 | .994 4714 ⁵⁷⁸ | 1038 ¹¹ |
| .143 | .996 9329 ⁴³⁰ | 0580 ⁸ | .193 | .994 4136 ⁵⁸⁰ | 1049 ¹⁰ |
| .144 | .996 8899 ⁴³³ | 0588 ⁸ | .194 | .994 3556 ⁵⁸³ | 1059 ¹¹ |
| 0.145 | 0.996 8466 ⁴³⁷ | 0.000 0596 ⁸ | 0.195 | 0.994 2973 ⁵⁸⁶ | 0.000 1070 ¹¹ |
| .146 | .996 8029 ⁴³⁹ | 0604 ⁸ | .196 | .994 2387 ⁵⁹⁰ | 1081 ¹¹ |
| .147 | .996 7590 ⁴⁴³ | 0612 ⁸ | .197 | .994 1797 ⁵⁹² | 1092 ¹¹ |
| .148 | .996 7147 ⁴⁴⁵ | 0620 ⁸ | .198 | .994 1205 ⁵⁹⁵ | 1103 ¹¹ |
| .149 | .996 6702 ⁴⁴⁸ | 0629 ⁸ | .199 | .994 0610 ⁵⁹⁹ | 1114 ¹¹ |
| 0.150 | 0.996 6254 | 0.000 0637 | 0.200 | 0.994 0011 | 0.000 1125 |

TABLE 3.

| $e^{\frac{1}{2}}\sigma$ | J | K | $e^{\frac{1}{2}}\sigma$ | J | K |
|-------------------------|--------------------------|--------------------|-------------------------|--------------------------|--------------------|
| 0.200 | 0.994 0011 | 0.000 1125 | 0.250 | 0.990 6278 | 0.000 1742 |
| .201 | .993 9410 ⁶⁰¹ | 1136 ¹¹ | .251 | .990 5527 ⁷⁵¹ | 1755 ¹³ |
| .202 | .993 8806 ⁶⁰⁴ | 1147 ¹¹ | .252 | .990 4773 ⁷⁵⁴ | 1769 ¹⁴ |
| .203 | .993 8199 ⁶⁰⁷ | 1158 ¹¹ | .253 | .990 4016 ⁷⁵⁷ | 1783 ¹⁴ |
| .204 | .993 7588 ⁶¹¹ | 1169 ¹¹ | .254 | .990 3256 ⁷⁶⁰ | 1796 ¹³ |
| | 613 | 12 | | 763 | 14 |
| 0.205 | 0.993 6975 | 0.000 1181 | 0.255 | 0.990 2493 | 0.000 1810 |
| .206 | .993 6359 ⁶¹⁶ | 1192 ¹¹ | .256 | .990 1727 ⁷⁶⁶ | 1824 ¹⁴ |
| .207 | .993 5740 ⁶¹⁹ | 1204 ¹² | .257 | .990 0958 ⁷⁶⁹ | 1838 ¹⁴ |
| .208 | .993 5117 ⁶²³ | 1215 ¹¹ | .258 | .990 0186 ⁷⁷² | 1852 ¹⁴ |
| .209 | .993 4492 ⁶²⁵ | 1226 ¹¹ | .259 | .989 9411 ⁷⁷⁵ | 1866 ¹⁴ |
| | 628 | 12 | | 778 | 14 |
| 0.210 | 0.993 3864 | 0.000 1238 | 0.260 | 0.989 8633 | 0.000 1880 |
| .211 | .993 3233 ⁶³¹ | 1250 ¹² | .261 | .989 7852 ⁷⁸¹ | 1894 ¹⁴ |
| .212 | .993 2598 ⁶³⁵ | 1261 ¹¹ | .262 | .989 7068 ⁷⁸⁴ | 1908 ¹⁴ |
| .213 | .993 1961 ⁶³⁷ | 1273 ¹² | .263 | .989 6281 ⁷⁸⁷ | 1922 ¹⁴ |
| .214 | .993 1321 ⁶⁴⁰ | 1285 ¹² | .264 | .989 5491 ⁷⁹⁰ | 1936 ¹⁴ |
| | 643 | 12 | | 793 | 15 |
| 0.215 | 0.993 0678 | 0.000 1297 | 0.265 | 0.989 4698 | 0.000 1951 |
| .216 | .993 0032 ⁶⁴⁶ | 1308 ¹¹ | .266 | .989 3902 ⁷⁹⁶ | 1965 ¹⁴ |
| .217 | .992 9382 ⁶⁵⁰ | 1320 ¹² | .267 | .989 3103 ⁷⁹⁹ | 1979 ¹⁴ |
| .218 | .992 8730 ⁶⁵² | 1332 ¹² | .268 | .989 2301 ⁸⁰² | 1994 ¹⁵ |
| .219 | .992 8075 ⁶⁵⁵ | 1344 ¹² | .269 | .989 1496 ⁸⁰⁵ | 2008 ¹⁴ |
| | 658 | 12 | | 808 | 15 |
| 0.220 | 0.992 7417 | 0.000 1356 | 0.270 | 0.989 0688 | 0.000 2023 |
| .221 | .992 6756 ⁶⁶¹ | 1369 ¹³ | .271 | .988 9877 ⁸¹¹ | 2037 ¹⁵ |
| .222 | .992 6091 ⁶⁶⁵ | 1381 ¹² | .272 | .988 9063 ⁸¹⁴ | 2052 ¹⁴ |
| .223 | .992 5424 ⁶⁶⁷ | 1393 ¹² | .273 | .988 8246 ⁸¹⁷ | 2067 ¹⁵ |
| .224 | .992 4754 ⁶⁷⁰ | 1405 ¹² | .274 | .988 7426 ⁸²⁰ | 2081 ¹⁴ |
| | 673 | 12 | | 822 | 15 |
| 0.225 | 0.992 4081 | 0.000 1417 | 0.275 | 0.988 6604 | 0.000 2096 |
| .226 | .992 3405 ⁶⁷⁶ | 1430 ¹³ | .276 | .988 5778 ⁸²⁶ | 2111 ¹⁵ |
| .227 | .992 2726 ⁶⁷⁹ | 1442 ¹² | .277 | .988 4949 ⁸²⁹ | 2126 ¹⁵ |
| .228 | .992 2043 ⁶⁸³ | 1455 ¹³ | .278 | .988 4117 ⁸³² | 2141 ¹⁵ |
| .229 | .992 1358 ⁶⁸⁵ | 1467 ¹² | .279 | .988 3282 ⁸³⁵ | 2156 ¹⁵ |
| | 688 | 13 | | 838 | 14 |
| 0.230 | 0.992 0670 | 0.000 1480 | 0.280 | 0.988 2444 | 0.000 2170 |
| .231 | .991 9979 ⁶⁹¹ | 1492 ¹² | .281 | .988 1603 ⁸⁴¹ | 2186 ¹⁶ |
| .232 | .991 9285 ⁶⁹⁴ | 1505 ¹³ | .282 | .988 0759 ⁸⁴⁴ | 2201 ¹⁵ |
| .233 | .991 8588 ⁶⁹⁷ | 1518 ¹³ | .283 | .987 9913 ⁸⁴⁶ | 2216 ¹⁵ |
| .234 | .991 7887 ⁷⁰¹ | 1531 ¹³ | .284 | .987 9063 ⁸⁵⁰ | 2231 ¹⁵ |
| | 703 | 12 | | 853 | 15 |
| 0.235 | 0.991 7184 | 0.000 1543 | 0.285 | 0.987 8210 | 0.000 2246 |
| .236 | .991 6478 ⁷⁰⁶ | 1556 ¹³ | .286 | .987 7354 ⁸⁵⁶ | 2261 ¹⁵ |
| .237 | .991 5769 ⁷⁰⁹ | 1569 ¹³ | .287 | .987 6496 ⁸⁵⁹ | 2277 ¹⁶ |
| .238 | .991 5057 ⁷¹² | 1582 ¹³ | .288 | .987 5633 ⁸⁶² | 2292 ¹⁵ |
| .239 | .991 4342 ⁷¹⁵ | 1595 ¹³ | .289 | .987 4769 ⁸⁶⁴ | 2307 ¹⁶ |
| | 718 | 13 | | 868 | 16 |
| 0.240 | 0.991 3624 | 0.000 1608 | 0.290 | 0.987 3901 | 0.000 2323 |
| .241 | .991 2903 ⁷²¹ | 1621 ¹³ | .291 | .987 3036 ⁸⁷¹ | 2338 ¹⁵ |
| .242 | .991 2179 ⁷²⁴ | 1634 ¹³ | .292 | .987 2156 ⁸⁷⁴ | 2354 ¹⁵ |
| .243 | .991 1451 ⁷²⁸ | 1648 ¹⁴ | .293 | .987 1279 ⁸⁷⁷ | 2369 ¹⁵ |
| .244 | .991 0721 ⁷³⁰ | 1661 ¹³ | .294 | .987 0400 ⁸⁷⁹ | 2385 ¹⁶ |
| | 733 | 13 | | 883 | 16 |
| 0.245 | 0.990 9988 | 0.000 1674 | 0.295 | 0.986 9517 | 0.000 2401 |
| .246 | .990 9252 ⁷³⁶ | 1688 ¹⁴ | .296 | .986 8631 ⁸⁸⁶ | 2416 ¹⁵ |
| .247 | .990 8513 ⁷³⁹ | 1701 ¹³ | .297 | .986 7742 ⁸⁸⁹ | 2432 ¹⁶ |
| .248 | .990 7771 ⁷⁴² | 1715 ¹⁴ | .298 | .986 6851 ⁸⁹¹ | 2448 ¹⁶ |
| .249 | .990 7026 ⁷⁴⁵ | 1728 ¹³ | .299 | .986 5956 ⁸⁹⁵ | 2464 ¹⁶ |
| | 748 | 14 | | 898 | 16 |
| 0.250 | 0.990 6278 | 0.000 1742 | 0.300 | 0.986 5058 | 0.000 2480 |

TABLE 3.

| $\epsilon^{\frac{1}{2}}\sigma$ | J | K | $\epsilon^{\frac{1}{2}}\sigma$ | J | K |
|--------------------------------|---------------------------|--------------------|--------------------------------|---------------------------|--------------------|
| 0.300 | 0.986 5058 | 0.000 2480 | 0.350 | 0.981 6358 | 0.000 3330 |
| .301 | .986 4157 ⁹⁰¹ | 2496 ¹⁶ | .351 | .981 5308 ¹⁰⁵⁰ | 3348 ¹⁸ |
| .302 | .986 3254 ⁹⁰³ | 2512 ¹⁶ | .352 | .981 4254 ¹⁰⁵⁴ | 3366 ¹⁸ |
| .303 | .986 2347 ⁹⁰⁷ | 2528 ¹⁶ | .353 | .981 3198 ¹⁰⁵⁶ | 3384 ¹⁸ |
| .304 | .986 1437 ⁹¹⁰ | 2544 ¹⁶ | .354 | .981 2139 ¹⁰⁵⁹ | 3402 ¹⁸ |
| | | | | | 3421 ¹⁹ |
| 0.305 | 0.986 0525 | 0.000 2560 | 0.355 | 0.981 1077 | 0.000 3421 |
| .306 | .985 9609 ⁹¹⁶ | 2576 ¹⁶ | .356 | .981 0012 ¹⁰⁶⁵ | 3439 ¹⁸ |
| .307 | .985 8690 ⁹¹⁹ | 2592 ¹⁶ | .357 | .980 8943 ¹⁰⁶⁹ | 3457 ¹⁸ |
| .308 | .985 7769 ⁹²¹ | 2609 ¹⁷ | .358 | .980 7872 ¹⁰⁷¹ | 3476 ¹⁸ |
| .309 | .985 6844 ⁹²⁵ | 2625 ¹⁶ | .359 | .980 6798 ¹⁰⁷⁴ | 3494 ¹⁸ |
| | | | | | 3512 ¹⁹ |
| 0.310 | 0.985 5916 | 0.000 2641 | 0.360 | 0.980 5721 | 0.000 3512 |
| .311 | .985 4986 ⁹³⁰ | 2658 ¹⁷ | .361 | .980 4641 ¹⁰⁸⁰ | 3531 ¹⁸ |
| .312 | .985 4052 ⁹³⁴ | 2674 ¹⁶ | .362 | .980 3558 ¹⁰⁸³ | 3549 ¹⁸ |
| .313 | .985 3115 ⁹³⁷ | 2690 ¹⁶ | .363 | .980 2471 ¹⁰⁸⁷ | 3568 ¹⁹ |
| .314 | .985 2176 ⁹³⁹ | 2707 ¹⁷ | .364 | .980 1382 ¹⁰⁸⁹ | 3587 ¹⁸ |
| | | | | | 3605 ¹⁹ |
| 0.315 | 0.985 1233 | 0.000 2724 | 0.365 | 0.980 0290 | 0.000 3605 |
| .316 | .985 0288 ⁹⁴⁵ | 2740 ¹⁶ | .366 | .979 9195 ¹⁰⁹⁵ | 3624 ¹⁹ |
| .317 | .984 9339 ⁹⁴⁹ | 2757 ¹⁷ | .367 | .979 8097 ¹⁰⁹⁸ | 3643 ¹⁹ |
| .318 | .984 8387 ⁹⁵² | 2773 ¹⁶ | .368 | .979 6996 ¹¹⁰¹ | 3661 ¹⁸ |
| .319 | .984 7433 ⁹⁵⁴ | 2790 ¹⁷ | .369 | .979 5892 ¹¹⁰⁴ | 3680 ¹⁹ |
| | | | | | 3699 ¹⁹ |
| 0.320 | 0.984 6475 | 0.000 2807 | 0.370 | 0.979 4785 | 0.000 3699 |
| .321 | .984 5515 ⁹⁶⁰ | 2824 ¹⁷ | .371 | .979 3675 ¹¹¹⁰ | 3718 ¹⁹ |
| .322 | .984 4551 ⁹⁶⁴ | 2841 ¹⁷ | .372 | .979 2562 ¹¹¹³ | 3737 ¹⁹ |
| .323 | .984 3585 ⁹⁶⁶ | 2858 ¹⁷ | .373 | .979 1446 ¹¹¹⁶ | 3756 ¹⁹ |
| .324 | .984 2615 ⁹⁷⁰ | 2875 ¹⁷ | .374 | .979 0327 ¹¹¹⁹ | 3775 ¹⁹ |
| | | | | | 3794 ¹⁹ |
| 0.325 | 0.984 1643 | 0.000 2892 | 0.375 | 0.978 9205 | 0.000 3794 |
| .326 | .984 0667 ⁹⁷⁶ | 2909 ¹⁷ | .376 | .978 8080 ¹¹²⁵ | 3813 ¹⁹ |
| .327 | .983 9689 ⁹⁷⁸ | 2926 ¹⁷ | .377 | .978 6952 ¹¹²⁸ | 3832 ¹⁹ |
| .328 | .983 8707 ⁹⁸² | 2943 ¹⁷ | .378 | .978 5821 ¹¹³¹ | 3851 ¹⁹ |
| .329 | .983 7723 ⁹⁸⁴ | 2960 ¹⁷ | .379 | .978 4687 ¹¹³⁴ | 3870 ¹⁹ |
| | | | | | 3889 ¹⁹ |
| 0.330 | 0.983 6735 | 0.000 2977 | 0.380 | 0.978 3550 | 0.000 3889 |
| .331 | .983 5745 ⁹⁹⁰ | 2994 ¹⁷ | .381 | .978 2410 ¹¹⁴⁰ | 3908 ¹⁹ |
| .332 | .983 4751 ⁹⁹⁴ | 3012 ¹⁸ | .382 | .978 1267 ¹¹⁴³ | 3928 ²⁰ |
| .333 | .983 3755 ⁹⁹⁶ | 3029 ¹⁷ | .383 | .978 0121 ¹¹⁴⁶ | 3947 ¹⁹ |
| .334 | .983 2755 ¹⁰⁰⁰ | 3046 ¹⁷ | .384 | .977 8973 ¹¹⁴⁸ | 3966 ²⁰ |
| | | | | | 3986 ¹⁹ |
| 0.335 | 0.983 1753 | 0.000 3064 | 0.385 | 0.977 7821 | 0.000 3986 |
| .336 | .983 0748 ¹⁰⁰⁵ | 3081 ¹⁷ | .386 | .977 6666 ¹¹⁵⁵ | 4005 ²⁰ |
| .337 | .982 9739 ¹⁰⁰⁹ | 3099 ¹⁸ | .387 | .977 5508 ¹¹⁵⁸ | 4025 ²⁰ |
| .338 | .982 8728 ¹⁰¹¹ | 3116 ¹⁸ | .388 | .977 4347 ¹¹⁶¹ | 4044 ¹⁹ |
| .339 | .982 7713 ¹⁰¹⁵ | 3134 ¹⁷ | .389 | .977 3183 ¹¹⁶⁴ | 4064 ²⁰ |
| | | | | | 4083 ²⁰ |
| 0.340 | 0.982 6696 | 0.000 3151 | 0.390 | 0.977 2017 | 0.000 4083 |
| .341 | .982 5676 ¹⁰²⁰ | 3169 ¹⁸ | .391 | .977 0847 ¹¹⁷⁰ | 4103 ¹⁹ |
| .342 | .982 4652 ¹⁰²⁴ | 3187 ¹⁸ | .392 | .976 9674 ¹¹⁷³ | 4122 ²⁰ |
| .343 | .982 3626 ¹⁰²⁶ | 3205 ¹⁸ | .393 | .976 8498 ¹¹⁷⁶ | 4142 ²⁰ |
| .344 | .982 2597 ¹⁰²⁹ | 3222 ¹⁷ | .394 | .976 7320 ¹¹⁷⁸ | 4162 ²⁰ |
| | | | | | 4182 ²⁰ |
| 0.345 | 0.982 1564 | 0.000 3240 | 0.395 | 0.976 6138 | 0.000 4182 |
| .346 | .982 0529 ¹⁰³⁵ | 3258 ¹⁸ | .396 | .976 4953 ¹¹⁸⁵ | 4201 ¹⁹ |
| .347 | .981 9491 ¹⁰³⁸ | 3276 ¹⁸ | .397 | .976 3766 ¹¹⁸⁷ | 4221 ²⁰ |
| .348 | .981 8449 ¹⁰⁴² | 3294 ¹⁸ | .398 | .976 2575 ¹¹⁹¹ | 4241 ²⁰ |
| .349 | .981 7405 ¹⁰⁴⁴ | 3312 ¹⁸ | .399 | .976 1381 ¹¹⁹⁴ | 4261 ²⁰ |
| | | | | | 4281 |
| 0.350 | 0.981 6358 | 0.000 3330 | 0.400 | 0.976 0184 | 0.000 4281 |

TABLE 3.

| $\epsilon^{\frac{1}{2}}\sigma$ | J | K | $\epsilon^{\frac{1}{2}}\sigma$ | J | K |
|--------------------------------|----------------------------|--------------------------|--------------------------------|----------------------------|--------------------------|
| 0.400 | 0.976 0184 | 0.000 4281 ₂₀ | 0.450 | 0.969 6546 ₁₃₄₉ | 0.000 5319 ₂₂ |
| .401 | .975 8985 ₁₁₉₉ | 4301 ₂₀ | .451 | .969 5197 ₁₃₅₁ | 5341 ₂₁ |
| .402 | .975 7782 ₁₂₀₃ | 4321 ₂₀ | .452 | .969 3846 ₁₃₅₅ | 5362 ₂₂ |
| .403 | .975 6577 ₁₂₀₅ | 4341 ₂₀ | .453 | .969 2491 ₁₃₅₈ | 5384 ₂₂ |
| .404 | .975 5368 ₁₂₁₂ | 4361 ₂₀ | .454 | .969 1133 ₁₃₆₁ | 5406 ₂₁ |
| 0.405 | 0.975 4156 ₁₂₁₄ | 0.000 4381 ₂₀ | 0.455 | .968 9772 ₁₃₆₄ | 0.000 5427 ₂₂ |
| .406 | .975 2942 ₁₂₁₈ | 4401 ₂₀ | .456 | .968 8408 ₁₃₆₆ | 5449 ₂₂ |
| .407 | .975 1724 ₁₂₂₀ | 4421 ₂₀ | .457 | .968 7042 ₁₃₇₀ | 5471 ₂₁ |
| .408 | .975 0504 ₁₂₂₄ | 4441 ₂₀ | .458 | .968 5672 ₁₃₇₃ | 5492 ₂₁ |
| .409 | .974 9280 ₁₂₂₆ | 4462 ₂₁ | .459 | .968 4299 ₁₃₇₅ | 5514 ₂₂ |
| 0.410 | 0.974 8054 ₁₂₃₀ | 0.000 4482 ₂₀ | 0.460 | 0.968 2924 ₁₃₇₉ | 0.000 5536 ₂₂ |
| .411 | .974 6824 ₁₂₃₂ | 4502 ₂₁ | .461 | .968 1545 ₁₃₈₂ | 5558 ₂₂ |
| .412 | .974 5592 ₁₂₃₆ | 4523 ₂₁ | .462 | .968 0163 ₁₃₈₄ | 5580 ₂₂ |
| .413 | .974 4356 ₁₂₃₈ | 4543 ₂₀ | .463 | .967 8779 ₁₃₈₈ | 5602 ₂₂ |
| .414 | .974 3118 ₁₂₄₂ | 4563 ₂₁ | .464 | .967 7391 ₁₃₉₀ | 5624 ₂₂ |
| 0.415 | 0.974 1876 ₁₂₄₄ | 0.000 4584 ₂₀ | 0.465 | 0.967 6001 ₁₃₉₄ | 0.000 5646 ₂₂ |
| .416 | .974 0632 ₁₂₄₇ | 4604 ₂₁ | .466 | .967 4607 ₁₃₉₇ | 5668 ₂₂ |
| .417 | .973 9385 ₁₂₅₁ | 4625 ₂₁ | .467 | .967 3210 ₁₃₉₉ | 5690 ₂₂ |
| .418 | .973 8134 ₁₂₅₃ | 4645 ₂₁ | .468 | .967 1811 ₁₄₀₃ | 5712 ₂₂ |
| .419 | .973 6881 ₁₂₅₇ | 4666 ₂₀ | .469 | .967 0408 ₁₄₀₅ | 5734 ₂₂ |
| 0.420 | 0.973 5624 ₁₂₅₉ | 0.000 4686 ₂₁ | 0.470 | 0.966 9003 ₁₄₀₉ | 0.000 5756 ₂₂ |
| .421 | .973 4365 ₁₂₆₂ | 4707 ₂₁ | .471 | .966 7594 ₁₄₁₁ | 5778 ₂₂ |
| .422 | .973 3103 ₁₂₆₆ | 4728 ₂₀ | .472 | .966 6183 ₁₄₁₄ | 5800 ₂₂ |
| .423 | .973 1837 ₁₂₆₈ | 4748 ₂₁ | .473 | .966 4769 ₁₄₁₈ | 5822 ₂₂ |
| .424 | .973 0569 ₁₂₇₁ | 4769 ₂₁ | .474 | .966 3351 ₁₄₂₀ | 5844 ₂₃ |
| 0.425 | 0.972 9298 ₁₂₇₄ | 0.000 4790 ₂₁ | 0.475 | 0.966 1931 ₁₄₂₄ | 0.000 5867 ₂₂ |
| .426 | .972 8024 ₁₂₇₈ | 4811 ₂₁ | .476 | .966 0507 ₁₄₂₆ | 5889 ₂₂ |
| .427 | .972 6746 ₁₂₈₀ | 4832 ₂₀ | .477 | .965 9081 ₁₄₂₉ | 5911 ₂₂ |
| .428 | .972 5466 ₁₂₈₃ | 4852 ₂₁ | .478 | .965 7652 ₁₄₃₃ | 5933 ₂₃ |
| .429 | .972 4183 ₁₂₈₆ | 4873 ₂₁ | .479 | .965 6219 ₁₄₃₅ | 5956 ₂₂ |
| 0.430 | 0.972 2897 ₁₂₈₉ | 0.000 4894 ₂₁ | 0.480 | 0.965 4784 ₁₄₃₈ | 0.000 5978 ₂₂ |
| .431 | .972 1608 ₁₂₉₃ | 4915 ₂₁ | .481 | .965 3346 ₁₄₄₁ | 6000 ₂₃ |
| .432 | .972 0315 ₁₂₉₅ | 4936 ₂₁ | .482 | .965 1905 ₁₄₄₅ | 6023 ₂₂ |
| .433 | .971 9020 ₁₂₉₈ | 4957 ₂₁ | .483 | .965 0460 ₁₄₄₇ | 6045 ₂₂ |
| .434 | .971 7722 ₁₃₀₁ | 4978 ₂₁ | .484 | .964 9013 ₁₄₅₀ | 6068 ₂₃ |
| 0.435 | 0.971 6421 ₁₃₀₄ | 0.000 4999 ₂₁ | 0.485 | 0.964 7563 ₁₄₅₃ | 0.000 6090 ₂₃ |
| .436 | .971 5117 ₁₃₀₇ | 5020 ₂₂ | .486 | .964 6110 ₁₄₅₆ | 6113 ₂₃ |
| .437 | .971 3810 ₁₃₁₀ | 5042 ₂₁ | .487 | .964 4654 ₁₄₅₉ | 6135 ₂₂ |
| .438 | .971 2500 ₁₃₁₃ | 5063 ₂₁ | .488 | .964 3195 ₁₄₆₃ | 6158 ₂₃ |
| .439 | .971 1187 ₁₃₁₆ | 5084 ₂₁ | .489 | .964 1732 ₁₄₆₅ | 6180 ₂₃ |
| 0.440 | 0.970 9871 ₁₃₁₉ | 0.000 5105 ₂₁ | 0.490 | 0.964 0267 ₁₄₆₈ | 0.000 6203 ₂₃ |
| .441 | .970 8552 ₁₃₂₂ | 5126 ₂₂ | .491 | .963 8799 ₁₄₇₁ | 6226 ₂₂ |
| .442 | .970 7230 ₁₃₂₅ | 5148 ₂₂ | .492 | .963 7328 ₁₄₇₄ | 6248 ₂₂ |
| .443 | .970 5905 ₁₃₂₈ | 5169 ₂₁ | .493 | .963 5854 ₁₄₇₇ | 6271 ₂₃ |
| .444 | .970 4577 ₁₃₃₁ | 5190 ₂₂ | .494 | .963 4377 ₁₄₈₀ | 6293 ₂₂ |
| 0.445 | 0.970 3246 ₁₃₃₄ | 0.000 5212 ₂₁ | 0.495 | 0.963 2897 ₁₄₈₃ | 0.000 6316 ₂₃ |
| .446 | .970 1912 ₁₃₃₇ | 5233 ₂₂ | .496 | .963 1414 ₁₄₈₆ | 6339 ₂₃ |
| .447 | .970 0575 ₁₃₄₀ | 5255 ₂₁ | .497 | .962 9928 ₁₄₈₉ | 6362 ₂₂ |
| .448 | .969 9235 ₁₃₄₃ | 5276 ₂₂ | .498 | .962 8439 ₁₄₉₁ | 6384 ₂₃ |
| .449 | .969 7892 ₁₃₄₆ | 5298 ₂₁ | .499 | .962 6946 ₁₄₉₃ | 6407 ₂₃ |
| 0.450 | 0.969 6546 | 0.000 5319 | 0.500 | 0.962 5453 | 0.000 6430 |

TABLE 3.

| $\epsilon\lambda\sigma$ | J | K | $\epsilon\lambda\sigma$ | J | K |
|-------------------------|----------------------------|--------------------------|-------------------------|----------------------------|--------------------------|
| 0.500 | 0.962 5453 ¹⁴⁹⁸ | 0.000 6430 ²³ | 0.550 | 0.954 6915 ¹⁶⁴⁷ | 0.000 7596 ²⁴ |
| .501 | .962 3955 ¹⁵⁰¹ | 6453 ²³ | .551 | .954 5268 ¹⁶⁴⁹ | 7620 ²⁴ |
| .502 | .962 2454 ¹⁵⁰⁴ | 6476 ²³ | .552 | .954 3619 ¹⁶⁵³ | 7644 ²⁴ |
| .503 | .962 0950 ¹⁵⁰⁶ | 6499 ²³ | .553 | .954 1966 ¹⁶⁵⁵ | 7668 ²⁴ |
| .504 | .961 9444 ¹⁵¹⁰ | 6522 ²³ | .554 | .954 0311 ¹⁶⁵⁹ | 7692 ²⁴ |
| 0.505 | 0.961 7934 ¹⁵¹³ | 0.000 6545 ²² | 0.555 | 0.953 8652 ¹⁶⁶¹ | 0.000 7715 ²⁴ |
| .506 | .961 6421 ¹⁵¹⁶ | 6567 ²³ | .556 | .953 6991 ¹⁶⁶⁵ | 7739 ²⁴ |
| .507 | .961 4905 ¹⁵¹⁸ | 6590 ²³ | .557 | .953 5326 ¹⁶⁶⁷ | 7763 ²⁴ |
| .508 | .961 3387 ¹⁵²² | 6613 ²³ | .558 | .953 3659 ¹⁶⁷¹ | 7787 ²⁴ |
| .509 | .961 1865 ¹⁵²⁵ | 6636 ²³ | .559 | .953 1988 ¹⁶⁷³ | 7811 ²⁴ |
| 0.510 | 0.961 0340 ¹⁵²⁷ | 0.000 6659 ²⁴ | 0.560 | 0.953 0315 ¹⁶⁷⁶ | 0.000 7835 ²⁴ |
| .511 | .960 8813 ¹⁵³¹ | 6683 ²³ | .561 | .952 8639 ¹⁶⁸⁰ | 7859 ²³ |
| .512 | .960 7282 ¹⁵³³ | 6706 ²³ | .562 | .952 6959 ¹⁶⁸² | 7882 ²⁴ |
| .513 | .960 5749 ¹⁵³⁷ | 6729 ²³ | .563 | .952 5277 ¹⁶⁸⁵ | 7906 ²⁴ |
| .514 | .960 4212 ¹⁵⁴⁰ | 6752 ²³ | .564 | .952 3592 ¹⁶⁸⁸ | 7930 ²⁴ |
| 0.515 | 0.960 2672 ¹⁵⁴² | 0.000 6775 ²³ | 0.565 | 0.952 1904 ¹⁶⁹² | 0.000 7954 ²⁴ |
| .516 | .960 1130 ¹⁵⁴⁵ | 6798 ²³ | .566 | .952 0212 ¹⁶⁹⁴ | 7978 ²⁴ |
| .517 | .959 9585 ¹⁵⁴⁹ | 6821 ²⁴ | .567 | .951 8518 ¹⁶⁹⁷ | 8002 ²⁴ |
| .518 | .959 8036 ¹⁵⁵¹ | 6845 ²³ | .568 | .951 6821 ¹⁷⁰⁰ | 8026 ²⁴ |
| .519 | .959 6485 ¹⁵⁵⁵ | 6868 ²³ | .569 | .951 5121 ¹⁷⁰³ | 8050 ²⁴ |
| 0.520 | 0.959 4930 ¹⁵⁵⁷ | 0.000 6891 ²³ | 0.570 | 0.951 3418 ¹⁷⁰⁶ | 0.000 8074 ²⁴ |
| .521 | .959 3373 ¹⁵⁶⁰ | 6914 ²³ | .571 | .951 1712 ¹⁷⁰⁹ | 8098 ²⁴ |
| .522 | .959 1813 ¹⁵⁶⁴ | 6938 ²³ | .572 | .951 0003 ¹⁷¹² | 8122 ²⁴ |
| .523 | .959 0249 ¹⁵⁶⁶ | 6961 ²³ | .573 | .950 8291 ¹⁷¹⁵ | 8146 ²⁴ |
| .524 | .958 8683 ¹⁵⁶⁹ | 6984 ²³ | .574 | .950 6576 ¹⁷¹⁸ | 8170 ²⁴ |
| 0.525 | 0.958 7114 ¹⁵⁷³ | 0.000 7007 ²⁴ | 0.575 | 0.950 4858 ¹⁷²¹ | 0.000 8194 ²⁴ |
| .526 | .958 5541 ¹⁵⁷⁵ | 7031 ²³ | .576 | .950 3137 ¹⁷²⁴ | 8218 ²⁴ |
| .527 | .958 3966 ¹⁵⁷⁸ | 7054 ²³ | .577 | .950 1413 ¹⁷²⁷ | 8243 ²⁵ |
| .528 | .958 2388 ¹⁵⁸¹ | 7078 ²³ | .578 | .949 9686 ¹⁷²⁹ | 8267 ²⁴ |
| .529 | .958 0807 ¹⁵⁸⁴ | 7101 ²³ | .579 | .949 7957 ¹⁷³³ | 8291 ²⁴ |
| 0.530 | 0.957 9223 ¹⁵⁸⁸ | 0.000 7124 ²⁴ | 0.580 | 0.949 6224 ¹⁷³⁶ | 0.000 8315 ²⁴ |
| .531 | .957 7635 ¹⁵⁹⁰ | 7148 ²³ | .581 | .949 4488 ¹⁷³⁹ | 8339 ²⁴ |
| .532 | .957 6045 ¹⁵⁹³ | 7171 ²³ | .582 | .949 2749 ¹⁷⁴¹ | 8363 ²⁴ |
| .533 | .957 4452 ¹⁵⁹⁶ | 7195 ²³ | .583 | .949 1008 ¹⁷⁴⁵ | 8387 ²⁴ |
| .534 | .957 2856 ¹⁵⁹⁹ | 7218 ²⁴ | .584 | .948 9263 ¹⁷⁴⁸ | 8411 ²⁵ |
| 0.535 | 0.957 1257 ¹⁶⁰² | 0.000 7242 ²³ | 0.585 | 0.948 7515 ¹⁷⁵⁰ | 0.000 8436 ²⁴ |
| .536 | .956 9655 ¹⁶⁰⁵ | 7265 ²³ | .586 | .948 5765 ¹⁷⁵⁴ | 8460 ²⁴ |
| .537 | .956 8050 ¹⁶⁰⁸ | 7289 ²³ | .587 | .948 4011 ¹⁷⁵⁶ | 8484 ²⁴ |
| .538 | .956 6442 ¹⁶¹¹ | 7312 ²³ | .588 | .948 2255 ¹⁷⁶⁰ | 8508 ²⁴ |
| .539 | .956 4831 ¹⁶¹⁴ | 7336 ²⁴ | .589 | .948 0495 ¹⁷⁶² | 8532 ²⁴ |
| 0.540 | 0.956 3217 ¹⁶¹⁷ | 0.000 7360 ²³ | 0.590 | 0.947 8733 ¹⁷⁶⁶ | 0.000 8556 ²⁵ |
| .541 | .956 1600 ¹⁶¹⁹ | 7383 ²³ | .591 | .947 6967 ¹⁷⁶⁸ | 8581 ²⁴ |
| .542 | .955 9981 ¹⁶²³ | 7407 ²⁴ | .592 | .947 5199 ¹⁷⁷² | 8605 ²⁴ |
| .543 | .955 8358 ¹⁶²⁶ | 7430 ²⁴ | .593 | .947 3427 ¹⁷⁷⁴ | 8629 ²⁴ |
| .544 | .955 6732 ¹⁶²⁹ | 7454 ²⁴ | .594 | .947 1653 ¹⁷⁷⁷ | 8653 ²⁵ |
| 0.545 | 0.955 5103 ¹⁶³¹ | 0.000 7478 ²³ | 0.595 | 0.946 9876 ¹⁷⁸¹ | 0.000 8678 ²⁴ |
| .546 | .955 3472 ¹⁶³⁵ | 7501 ²³ | .596 | .946 8095 ¹⁷⁸³ | 8702 ²⁴ |
| .547 | .955 1837 ¹⁶³⁸ | 7525 ²⁴ | .597 | .946 6312 ¹⁷⁸⁶ | 8726 ²⁴ |
| .548 | .955 0199 ¹⁶⁴¹ | 7549 ²⁴ | .598 | .946 4526 ¹⁷⁸⁹ | 8750 ²⁴ |
| .549 | .954 8558 ¹⁶⁴³ | 7573 ²³ | .599 | .946 2737 ¹⁷⁹² | 8774 ²⁵ |
| 0.550 | 0.954 6915 | 0.000 7596 | 0.600 | 0.946 0945 | 0.000 8799 |

TABLES FOR HYPERBOLIC MOTION.*

By HARLEY WOOD, M.Sc.

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In this article tables are given for the representation of hyperbolic Keplerian motion. They are based on the same formulæ, with the same numerical coefficients, prepared and intended for use in the same way as those in the previous article, "Tables for Nearly Parabolic Elliptic Motion" (Wood, 1951) and so only a few remarks need be added.

In order to avoid the use of imaginary arguments and give these tables a slightly different appearance from the previous ones we set $\alpha = -\epsilon = (e-1)/(e+1)$. The arguments for the respective tables then become $\alpha^{\frac{1}{2}}\mu$, α and $\alpha^{\frac{1}{2}}\sigma$.

A was calculated from the series when $\alpha^{\frac{1}{2}}\mu \leq 0.20$ and thereafter by obtaining $\sinh^{-1} \alpha^{\frac{1}{2}}\mu = \log\{\alpha^{\frac{1}{2}}\mu + (\alpha\mu^2 + 1)^{\frac{1}{2}}\}$ with the *Table of Natural Logarithms* of the "Federal Works Agency" (1941).

The signs of both h and K become negative for $e > 1$ (ϵ negative) but since only their product appears in the formula they are tabulated as positive.

Using the manuscript tables to two places beyond what are recorded here the values of R for the hyperbolic case were calculated from equation (4) of the previous article, μ first having been obtained from equation (2). The intervals of α and $\alpha^{\frac{1}{2}}\sigma$ at which this was done were the same as before and the greatest value of R obtained was 8 units of the ninth decimal place. R is again negligible in seven figure work.

REFERENCES.

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- Wood, H., 1951. *THIS JOURNAL*, **84**, 134. Also Sydney Obs. Papers No. 14.

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TABLE 1.

| $\alpha^{\frac{1}{2}}\mu$ | A | I | N | $\alpha^{\frac{1}{2}}\mu$ | A | I | N |
|---------------------------|--------------------------|---------------------|------------|---------------------------|-------------------------|-------------------|-------------------------|
| | | | | | 0. | 2. | 0. |
| 0.000 | 1.000 0000 | 3.0000 ⁰ | 1.000 0000 | 0.050 | 9988 767 | 9944 ² | 9993 758 |
| .001 | 0.999 9996 ⁴ | .0000 ⁰ | 0.999 9998 | .051 | 9988 314 ⁴⁵³ | 9942 ² | 9993 506 ²⁵² |
| .002 | .999 9982 ¹⁴ | .0000 ⁰ | .999 9990 | .052 | 9987 852 ⁴⁶² | 9939 ³ | 9993 249 ²⁵⁷ |
| .003 | .999 9960 ²² | .0000 ⁰ | .999 9978 | .053 | 9987 381 ⁴⁷¹ | 9937 ² | 9992 987 ²⁶² |
| .004 | .999 9928 ³² | 3.0000 ⁰ | .999 9960 | .054 | 9986 901 ⁴⁸⁰ | 9935 ³ | 9992 721 ²⁶⁶ |
| | | | | | | | 272 |
| 0.005 | 0.999 9888 | 2.9999 ⁰ | 0.999 9938 | 0.055 | 9986 412 | 9932 ² | 9992 449 |
| .006 | .999 9838 ⁵⁰ | .9999 ⁰ | .999 9910 | .056 | 9985 914 ⁴⁹⁸ | 9930 ² | 9992 172 ²⁷⁷ |
| .007 | .999 9780 ⁵⁸ | .9999 ⁰ | .999 9878 | .057 | 9985 408 ⁵⁰⁶ | 9927 ³ | 9991 891 ²⁸¹ |
| .008 | .999 9712 ⁶⁸ | .9999 ⁰ | .999 9840 | .058 | 9984 892 ⁵¹⁶ | 9925 ² | 9991 604 ²⁸⁷ |
| .009 | .999 9636 ⁷⁶ | .9998 ¹ | .999 9798 | .059 | 9984 368 ⁵²⁴ | 9922 ³ | 9991 313 ²⁹¹ |
| | | | | | | | 297 |
| 0.010 | 0.999 9550 | 2.9998 ¹ | 0.999 9750 | 0.060 | 9983 835 | 9919 ² | 9991 016 |
| .011 | .999 9456 ⁹⁴ | .9997 ¹ | .999 9698 | .061 | 9983 292 ⁵⁴³ | 9917 ³ | 9990 715 ³⁰¹ |
| .012 | .999 9352 ¹⁰⁴ | .9997 ⁰ | .999 9640 | .062 | 9982 741 ⁵⁵¹ | 9914 ³ | 9990 408 ³⁰⁷ |
| .013 | .999 9240 ¹¹² | .9996 ⁰ | .999 9578 | .063 | 9982 182 ⁵⁵⁹ | 9911 ³ | 9990 097 ³¹¹ |
| .014 | .999 9118 ¹²² | .9996 ⁰ | .999 9510 | .064 | 9981 613 ⁵⁶⁹ | 9908 ³ | 9989 781 ³¹⁶ |
| | | | | | | | 321 |
| 0.015 | 0.999 8988 | 2.9995 ¹ | 0.999 9438 | 0.065 | 9981 035 | 9905 ² | 9989 460 |
| .016 | .999 8848 ¹⁴⁰ | .9994 ⁰ | .999 9360 | .066 | 9980 449 ⁵⁸⁶ | 9902 ³ | 9989 134 ³²⁶ |
| .017 | .999 8700 ¹⁴⁸ | .9994 ⁰ | .999 9278 | .067 | 9979 853 ⁵⁹⁶ | 9899 ³ | 9988 803 ³³¹ |
| .018 | .999 8542 ¹⁵⁸ | .9993 ¹ | .999 9190 | .068 | 9979 249 ⁶⁰⁴ | 9896 ³ | 9988 467 ³³⁶ |
| .019 | .999 8376 ¹⁶⁶ | .9992 ¹ | .999 9098 | .069 | 9978 636 ⁶¹³ | 9893 ³ | 9988 126 ³⁴¹ |
| | | | | | | | 346 |
| 0.020 | 0.999 8200 | 2.9991 ¹ | 0.999 9000 | 0.070 | 9978 014 | 9890 ³ | 9987 780 |
| .021 | .999 8016 ¹⁸⁴ | .9990 ¹ | .999 8898 | .071 | 9977 383 ⁶³¹ | 9887 ³ | 9987 429 ³⁵¹ |
| .022 | .999 7823 ¹⁹³ | .9989 ¹ | .999 8790 | .072 | 9976 744 ⁶³⁹ | 9884 ³ | 9987 073 ³⁵⁶ |
| .023 | .999 7620 ²⁰³ | .9988 ¹ | .999 8678 | .073 | 9976 095 ⁶⁴⁹ | 9881 ³ | 9986 713 ³⁶⁰ |
| .024 | .999 7409 ²¹¹ | .9987 ¹ | .999 8560 | .074 | 9975 438 ⁶⁵⁷ | 9877 ³ | 9986 347 ³⁶⁶ |
| | | | | | | | 370 |
| 0.025 | 0.999 7189 | 2.9986 ¹ | 0.999 8438 | 0.075 | 9974 772 ⁶⁷⁵ | 9874 ³ | 9985 977 |
| .026 | .999 6959 ²³⁰ | .9985 ¹ | .999 8311 | .076 | 9974 097 ⁶⁸⁴ | 9871 ³ | 9985 602 ³⁷⁵ |
| .027 | .999 6721 ²³⁸ | .9984 ² | .999 8178 | .077 | 9973 413 ⁶⁹² | 9867 ⁴ | 9985 221 ³⁸¹ |
| .028 | .999 6474 ²⁴⁷ | .9982 ¹ | .999 8041 | .078 | 9972 721 ⁷⁰² | 9864 ³ | 9984 836 ³⁸⁵ |
| .029 | .999 6217 ²⁶⁵ | .9981 ¹ | .999 7898 | .079 | 9972 019 ⁷¹⁰ | 9860 ³ | 9984 446 ³⁹⁰ |
| | | | | | | | 395 |
| 0.030 | 0.999 5952 | 2.9980 ² | 0.999 7751 | 0.080 | 9971 309 | 9857 ⁴ | 9984 051 |
| .031 | .999 5678 ²⁷⁴ | .9978 ¹ | .999 7599 | .081 | 9970 590 ⁷¹⁹ | 9853 ³ | 9983 651 ⁴⁰⁰ |
| .032 | .999 5395 ²⁸³ | .9977 ¹ | .999 7441 | .082 | 9969 863 ⁷²⁷ | 9850 ³ | 9983 246 ⁴⁰⁵ |
| .033 | .999 5103 ²⁹² | .9976 ¹ | .999 7279 | .083 | 9969 126 ⁷³⁷ | 9846 ⁴ | 9982 837 ⁴⁰⁹ |
| .034 | .999 4802 ³⁰¹ | .9974 ² | .999 7112 | .084 | 9968 381 ⁷⁴⁵ | 9842 ⁴ | 9982 422 ⁴¹⁵ |
| | | | | | | | 420 |
| 0.035 | 0.999 4492 | 2.9972 ¹ | 0.999 6939 | 0.085 | 9967 627 ⁷⁶³ | 9838 ³ | 9982 002 |
| .036 | .999 4172 ³²⁰ | .9971 ¹ | .999 6762 | .086 | 9966 864 ⁷⁷² | 9835 ³ | 9981 578 ⁴²⁴ |
| .037 | .999 3845 ³²⁷ | .9969 ² | .999 6586 | .087 | 9966 092 ⁷⁸⁰ | 9831 ⁴ | 9981 149 ⁴²⁹ |
| .038 | .999 3508 ³³⁷ | .9968 ¹ | .999 6393 | .088 | 9965 312 ⁷⁸⁹ | 9827 ⁴ | 9980 715 ⁴³⁴ |
| .039 | .999 3162 ³⁴⁶ | .9966 ² | .999 6200 | .089 | 9964 523 ⁷⁹⁸ | 9823 ⁴ | 9980 276 ⁴³⁹ |
| | | | | | | | 444 |
| 0.040 | 0.999 2807 | 2.9964 ² | 0.999 6003 | 0.090 | 9963 725 | 9819 ⁴ | 9979 832 |
| .041 | .999 2443 ³⁶⁴ | .9962 ² | .999 5801 | .091 | 9962 918 ⁸⁰⁷ | 9815 ⁴ | 9979 383 ⁴⁴⁹ |
| .042 | .999 2070 ³⁷³ | .9960 ² | .999 5594 | .092 | 9962 103 ⁸¹⁵ | 9811 ⁴ | 9978 929 ⁴⁵⁴ |
| .043 | .999 1689 ³⁸¹ | .9958 ² | .999 5382 | .093 | 9961 279 ⁸²⁴ | 9807 ⁴ | 9978 470 ⁴⁵⁹ |
| .044 | .999 1298 ³⁹¹ | .9957 ² | .999 5165 | .094 | 9960 446 ⁸³³ | 9803 ⁵ | 9978 007 ⁴⁶³ |
| | | | | | | | 468 |
| 0.045 | 0.999 0898 | 2.9955 ³ | 0.999 4943 | 0.095 | 9959 604 ⁸⁵⁰ | 9798 ⁴ | 9977 539 |
| .046 | .999 0490 ⁴⁰⁸ | .9952 ² | .999 4716 | .096 | 9958 754 ⁸⁵⁹ | 9794 ⁴ | 9977 066 ⁴⁷³ |
| .047 | .999 0073 ⁴¹⁷ | .9950 ² | .999 4484 | .097 | 9957 895 ⁸⁶⁸ | 9790 ⁴ | 9976 588 ⁴⁷⁸ |
| .048 | .998 9646 ⁴²⁷ | .9948 ² | .999 4247 | .098 | 9957 027 ⁸⁷⁶ | 9786 ⁵ | 9976 105 ⁴⁸³ |
| .049 | .998 9211 ⁴³⁵ | .9946 ² | .999 4005 | .099 | 9956 151 ⁸⁸⁵ | 9781 ⁴ | 9975 617 ⁴⁸⁸ |
| | | | | | | | 493 |
| 0.050 | 0.998 8767 | 2.9944 | 0.999 3758 | 0.100 | 9955 266 | 9777 | 9975 124 |

TABLE 1.

| $\alpha^{\frac{1}{2}}\mu$ | A | I | N | $\alpha^{\frac{1}{2}}\mu$ | A | I | N |
|---------------------------|--------------------------|-------------------|-------------------------|---------------------------|--------------------------|-------------------|-------------------------|
| | 0. | 2. | 0. | | 0. | 2. | 0. |
| 0.100 | 9955 266 | 9777 | 9975 124 | 0.150 | 9900 086 | 9503 | 9944 374 |
| .101 | 9954 372 ⁸⁹⁴ | 9772 ⁵ | 9974 627 ⁴⁹⁷ | .151 | 9898 767 ¹³¹⁹ | 9497 ⁶ | 9943 638 ⁷³⁶ |
| .102 | 9953 470 | 9768 ⁴ | 9974 124 ⁵⁰³ | .152 | 9897 440 ¹³²⁷ | 9490 ⁷ | 9942 898 ⁷⁴⁰ |
| .103 | 9952 559 | 9763 ⁵ | 9973 617 ⁵⁰⁷ | .153 | 9896 104 ¹³³⁶ | 9483 ⁷ | 9942 153 ⁷⁴⁵ |
| .104 | 9951 639 | 9759 ⁴ | 9973 105 ⁵¹² | .154 | 9894 761 ¹³⁴³ | 9477 ⁶ | 9941 403 ⁷⁵⁰ |
| | | | | | | | |
| 0.105 | 9950 711 | 9754 | 9972 588 | 0.155 | 9893 409 | 9470 | 9940 648 |
| .106 | 9949 774 | 9750 ⁴ | 9972 067 ⁵²¹ | .156 | 9892 049 ¹³⁶⁰ | 9463 ⁷ | 9939 889 ⁷⁵⁹ |
| .107 | 9948 828 | 9745 ⁵ | 9971 540 ⁵²⁷ | .157 | 9890 680 ¹³⁶⁹ | 9457 ⁶ | 9939 125 ⁷⁶⁴ |
| .108 | 9947 874 | 9740 ⁵ | 9971 009 ⁵³¹ | .158 | 9889 303 ¹³⁷⁷ | 9450 ⁷ | 9938 357 ⁷⁶⁸ |
| .109 | 9946 911 | 9735 ⁵ | 9970 473 ⁵³⁶ | .159 | 9887 919 ¹³⁸⁴ | 9443 ⁷ | 9937 584 ⁷⁷³ |
| | | | | | | | |
| 0.110 | 9945 939 | 9730 | 9969 932 | 0.160 | 9886 525 | 9436 | 9936 806 |
| .111 | 9944 959 | 9726 ⁴ | 9969 386 ⁵⁴⁶ | .161 | 9885 124 ¹⁴⁰¹ | 9429 ⁷ | 9936 024 ⁷⁸² |
| .112 | 9943 970 | 9721 ⁵ | 9968 835 ⁵⁵¹ | .162 | 9883 715 ¹⁴⁰⁹ | 9422 ⁷ | 9935 237 ⁷⁸⁷ |
| .113 | 9942 972 | 9716 ⁵ | 9968 280 ⁵⁵⁵ | .163 | 9882 297 ¹⁴¹⁸ | 9415 ⁷ | 9934 446 ⁷⁹¹ |
| .114 | 9941 966 ¹⁰⁰⁶ | 9711 ⁵ | 9967 719 ⁵⁶¹ | .164 | 9880 871 ¹⁴²⁶ | 9408 ⁷ | 9933 649 ⁷⁹⁷ |
| | | | | | | | |
| 0.115 | 9940 952 | 9706 | 9967 154 | 0.165 | 9879 437 | 9401 | 9932 849 |
| .116 | 9939 926 ¹⁰²³ | 9701 ⁵ | 9966 584 ⁵⁷⁰ | .166 | 9877 995 ¹⁴⁴² | 9394 ⁷ | 9932 043 ⁸⁰⁶ |
| .117 | 9938 897 | 9695 ⁶ | 9966 010 ⁵⁷⁴ | .167 | 9876 544 ¹⁴⁵¹ | 9387 ⁷ | 9931 233 ⁸¹⁰ |
| .118 | 9937 856 ¹⁰⁴¹ | 9690 ⁵ | 9965 430 ⁵⁸⁰ | .168 | 9875 086 ¹⁴⁵⁸ | 9380 ⁷ | 9930 419 ⁸¹⁴ |
| .119 | 9936 808 ¹⁰⁴⁸ | 9685 ⁵ | 9964 846 ⁵⁸⁴ | .169 | 9873 619 ¹⁴⁶⁷ | 9372 ⁸ | 9929 599 ⁸²⁰ |
| | | | | | | | |
| 0.120 | 9935 750 | 9680 | 9964 257 | 0.170 | 9872 144 | 9365 | 9928 776 |
| .121 | 9934 684 ¹⁰⁶⁰ | 9675 ⁵ | 9963 663 ⁵⁹⁴ | .171 | 9870 661 ¹⁴⁸³ | 9358 ⁷ | 9927 947 ⁸²⁹ |
| .122 | 9933 609 | 9669 ⁶ | 9963 064 ⁵⁹⁹ | .172 | 9869 170 ¹⁴⁹¹ | 9350 ⁸ | 9927 114 ⁸³³ |
| .123 | 9932 526 ¹⁰⁸³ | 9664 ⁶ | 9962 461 ⁶⁰³ | .173 | 9867 671 ¹⁴⁹⁹ | 9343 ⁷ | 9926 277 ⁸³⁷ |
| .124 | 9931 435 ¹⁰⁹¹ | 9658 ⁶ | 9961 853 ⁶⁰⁸ | .174 | 9866 164 ¹⁵⁰⁷ | 9336 ⁸ | 9925 435 ⁸⁴² |
| | | | | | | | |
| 0.125 | 9930 335 | 9653 | 9961 240 | 0.175 | 9864 648 | 9328 | 9924 588 |
| .126 | 9929 226 ¹¹⁰⁹ | 9647 ⁶ | 9960 622 ⁶¹⁸ | .176 | 9863 125 ¹⁵²³ | 9321 ⁷ | 9923 737 ⁸⁵¹ |
| .127 | 9928 109 ¹¹¹⁷ | 9642 ⁵ | 9959 999 ⁶²³ | .177 | 9861 594 ¹⁵³¹ | 9313 ⁸ | 9922 881 ⁸⁵⁶ |
| .128 | 9926 983 ¹¹²⁶ | 9636 ⁶ | 9959 372 ⁶²⁷ | .178 | 9860 054 ¹⁵⁴⁰ | 9305 ⁸ | 9922 021 ⁸⁶⁰ |
| .129 | 9925 849 ¹¹³⁴ | 9631 ⁶ | 9958 740 ⁶³² | .179 | 9858 507 ¹⁵⁴⁷ | 9298 ⁸ | 9921 156 ⁸⁶⁵ |
| | | | | | | | |
| 0.130 | 9924 706 | 9625 | 9958 103 | 0.180 | 9856 951 | 9290 | 9920 286 |
| .131 | 9923 555 ¹¹⁵¹ | 9619 ⁶ | 9957 462 ⁶⁴¹ | .181 | 9855 388 ¹⁵⁶³ | 9282 ⁸ | 9919 412 ⁸⁷⁴ |
| .132 | 9922 396 ¹¹⁵⁹ | 9614 ⁵ | 9956 815 ⁶⁴⁷ | .182 | 9853 816 ¹⁵⁷² | 9275 ⁷ | 9918 534 ⁸⁷⁸ |
| .133 | 9921 228 ¹¹⁶⁸ | 9608 ⁶ | 9956 164 ⁶⁵¹ | .183 | 9852 237 ¹⁵⁷⁹ | 9267 ⁸ | 9917 651 ⁸⁸³ |
| .134 | 9920 051 ¹¹⁷⁷ | 9602 ⁶ | 9955 509 ⁶⁵⁵ | .184 | 9850 649 ¹⁵⁸⁸ | 9259 ⁸ | 9916 763 ⁸⁸⁸ |
| | | | | | | | |
| 0.135 | 9918 866 | 9596 | 9954 848 | 0.185 | 9849 054 | 9251 | 9915 871 |
| .136 | 9917 673 ¹¹⁹³ | 9590 ⁶ | 9954 183 ⁶⁶⁵ | .186 | 9847 450 ¹⁶⁰⁴ | 9243 ⁸ | 9914 975 ⁸⁹⁶ |
| .137 | 9916 471 ¹²⁰² | 9584 ⁶ | 9953 513 ⁶⁷⁰ | .187 | 9845 839 ¹⁶¹¹ | 9235 ⁸ | 9914 073 ⁹⁰² |
| .138 | 9915 261 ¹²¹⁰ | 9578 ⁶ | 9952 838 ⁶⁷⁵ | .188 | 9844 220 ¹⁶¹⁹ | 9227 ⁸ | 9913 168 ⁹⁰⁵ |
| .139 | 9914 042 ¹²¹⁹ | 9572 ⁶ | 9952 159 ⁶⁷⁹ | .189 | 9842 592 ¹⁶²⁸ | 9219 ⁸ | 9912 258 ⁹¹⁰ |
| | | | | | | | |
| 0.140 | 9912 815 | 9566 | 9951 474 | 0.190 | 9840 957 | 9211 | 9911 343 |
| .141 | 9911 580 ¹²³⁵ | 9560 ⁶ | 9950 786 ⁶⁸⁸ | .191 | 9839 314 ¹⁶⁴³ | 9203 ⁸ | 9910 424 ⁹¹⁹ |
| .142 | 9910 336 ¹²⁴⁴ | 9554 ⁶ | 9950 092 ⁶⁹⁴ | .192 | 9837 663 ¹⁶⁵¹ | 9195 ⁸ | 9909 501 ⁹²³ |
| .143 | 9909 084 ¹²⁵² | 9548 ⁶ | 9949 394 ⁶⁹⁸ | .193 | 9836 004 ¹⁶⁵⁹ | 9187 ⁸ | 9908 572 ⁹²⁹ |
| .144 | 9907 824 ¹²⁶⁰ | 9541 ⁷ | 9948 691 ⁷⁰³ | .194 | 9834 338 ¹⁶⁶⁶ | 9179 ⁸ | 9907 640 ⁹³² |
| | | | | | | | |
| 0.145 | 9906 555 | 9535 | 9947 983 | 0.195 | 9832 663 | 9171 | 9906 703 |
| .146 | 9905 278 ¹²⁷⁷ | 9529 ⁶ | 9947 271 ⁷¹² | .196 | 9830 980 ¹⁶⁸³ | 9162 ⁹ | 9905 762 ⁹⁴¹ |
| .147 | 9903 992 ¹²⁸⁶ | 9522 ⁷ | 9946 553 ⁷¹⁸ | .197 | 9829 290 ¹⁶⁹⁰ | 9154 ⁸ | 9904 816 ⁹⁴⁶ |
| .148 | 9902 698 ¹²⁹⁴ | 9516 ⁶ | 9945 832 ⁷²¹ | .198 | 9827 592 ¹⁶⁹⁸ | 9146 ⁸ | 9903 865 ⁹⁵¹ |
| .149 | 9901 396 ¹³⁰² | 9510 ⁶ | 9945 105 ⁷²⁷ | .199 | 9825 886 ¹⁷⁰⁶ | 9137 ⁹ | 9902 911 ⁹⁵⁴ |
| | | | | | | | |
| 0.150 | 9900 086 | 9503 | 9944 374 | 0.200 | 9824 172 | 9129 | 9901 951 |

TABLE I.

| $\alpha^{\frac{1}{2}}\mu$ | A | I | N | $\alpha^{\frac{1}{2}}\mu$ | A | I | N |
|---------------------------|--------------------------|--------------------|--------------------------|---------------------------|--------------------------|--------------------|--------------------------|
| | 0. | 2. | 0. | | 0. | 2. | 0. |
| 0.200 | 9824 172 | 9129 | 9901 951 | 0.250 | 9728 788 | 8663 ¹⁰ | 9848 450 ¹¹⁷⁸ |
| .201 | 9822 451 ¹⁷²¹ | 9121 ⁸ | 9900 988 ⁹⁶⁸ | .251 | 9726 691 ²⁰⁹⁷ | 8653 ¹⁰ | 9847 272 ¹¹⁸³ |
| .202 | 9820 722 ¹⁷²⁹ | 9112 ⁸ | 9900 020 ⁹⁷³ | .252 | 9724 588 ²¹⁰³ | 8643 ¹⁰ | 9846 089 ¹¹⁸⁶ |
| .203 | 9818 984 ¹⁷³⁸ | 9104 ⁸ | 9899 047 ⁹⁷⁷ | .253 | 9722 477 ²¹¹¹ | 8633 ¹⁰ | 9844 903 ¹¹⁹¹ |
| .204 | 9817 240 ¹⁷⁴⁴ | 9095 ⁹ | 9898 070 ⁹⁸¹ | .254 | 9720 360 ²¹¹⁷ | 8622 ¹¹ | 9843 712 ¹¹⁹⁵ |
| | | | | | | 2125 ¹⁰ | |
| 0.205 | 9815 487 | 9086 ⁸ | 9897 089 ⁹⁸⁶ | 0.255 | 9718 235 ²¹³² | 8612 ¹⁰ | 9842 517 ¹¹⁹⁹ |
| .206 | 9813 727 ¹⁷⁶⁰ | 9078 ⁸ | 9896 103 ⁹⁹⁰ | .256 | 9716 103 ²¹³⁹ | 8602 ¹¹ | 9841 318 ¹²⁰³ |
| .207 | 9811 958 ¹⁷⁶⁹ | 9069 ⁹ | 9895 113 ⁹⁹⁵ | .257 | 9713 964 ²¹⁴⁶ | 8591 ¹⁰ | 9840 115 ¹²⁰⁷ |
| .208 | 9810 183 ¹⁷⁷⁵ | 9060 ⁹ | 9894 118 ⁹⁹⁹ | .258 | 9711 818 ²¹⁵⁴ | 8581 ¹¹ | 9838 908 ¹²¹¹ |
| .209 | 9808 399 ¹⁷⁸⁴ | 9052 ⁹ | 9893 119 ¹⁰⁰³ | .259 | 9709 664 ²¹⁶⁰ | 8570 ¹⁰ | 9837 697 ¹²¹⁵ |
| | | | | | | | |
| 0.210 | 9806 608 | 9043 ⁹ | 9892 116 ¹⁰⁰⁸ | 0.260 | 9707 504 ²¹⁶⁷ | 8560 ¹¹ | 9836 482 ¹²²⁰ |
| .211 | 9804 809 ¹⁷⁹⁹ | 9034 ⁹ | 9891 108 ¹⁰¹² | .261 | 9705 337 ²¹⁷⁵ | 8549 ¹⁰ | 9835 262 ¹²²³ |
| .212 | 9803 002 ¹⁸⁰⁷ | 9025 ⁹ | 9890 096 ¹⁰¹⁶ | .262 | 9703 162 ²¹⁸¹ | 8539 ¹¹ | 9834 039 ¹²²⁸ |
| .213 | 9801 188 ¹⁸¹⁴ | 9016 ⁹ | 9889 080 ¹⁰²¹ | .263 | 9700 981 ²¹⁸⁹ | 8528 ¹⁰ | 9832 811 ¹²³¹ |
| .214 | 9799 366 ¹⁸²² | 9007 ⁹ | 9888 059 ¹⁰²⁵ | .264 | 9698 792 ²¹⁹⁵ | 8518 ¹¹ | 9831 580 ¹²³⁶ |
| | | | | | | | |
| 0.215 | 9797 537 | 8998 ⁹ | 9887 034 ¹⁰³⁰ | 0.265 | 9696 597 ²²⁰³ | 8507 ¹¹ | 9830 344 ¹²⁴⁰ |
| .216 | 9795 706 ¹⁸³⁷ | 8989 ⁹ | 9886 004 ¹⁰³⁴ | .266 | 9694 394 ²²⁰⁹ | 8496 ¹⁰ | 9829 104 ¹²⁴³ |
| .217 | 9793 855 ¹⁸⁴⁵ | 8980 ⁹ | 9884 970 ¹⁰³⁸ | .267 | 9692 185 ²²¹⁷ | 8486 ¹¹ | 9827 861 ¹²⁴⁸ |
| .218 | 9792 003 ¹⁸⁵² | 8971 ⁹ | 9883 932 ¹⁰⁴³ | .268 | 9689 968 ²²²³ | 8475 ¹⁰ | 9826 613 ¹²⁵² |
| .219 | 9790 143 ¹⁸⁶⁰ | 8962 ⁹ | 9882 889 ¹⁰⁴⁶ | .269 | 9687 745 ²²³⁰ | 8464 ¹¹ | 9825 361 ¹²⁵⁶ |
| | | | | | | | |
| 0.220 | 9788 275 | 8953 ⁹ | 9881 843 ¹⁰⁵² | 0.270 | 9685 515 ²²³⁸ | 8453 ¹⁰ | 9824 105 ¹²⁶⁰ |
| .221 | 9786 400 ¹⁸⁷⁵ | 8944 ⁹ | 9880 791 ¹⁰⁵⁵ | .271 | 9683 277 ²²⁴⁴ | 8443 ¹¹ | 9822 845 ¹²⁶⁴ |
| .222 | 9784 517 ¹⁸⁸³ | 8935 ⁹ | 9879 736 ¹⁰⁶⁰ | .272 | 9681 033 ²²⁵¹ | 8432 ¹⁰ | 9821 581 ¹²⁶⁸ |
| .223 | 9782 627 ¹⁸⁹⁰ | 8926 ⁹ | 9878 676 ¹⁰⁶⁴ | .273 | 9678 782 ²²⁵⁸ | 8421 ¹¹ | 9820 313 ¹²⁷² |
| .224 | 9780 730 ¹⁸⁹⁷ | 8916 ¹⁰ | 9877 612 ¹⁰⁶⁹ | .274 | 9676 524 ²²⁶⁴ | 8410 ¹¹ | 9819 041 ¹²⁷⁶ |
| | | | | | | | |
| 0.225 | 9778 824 | 8907 ⁹ | 9876 543 ¹⁰⁷³ | 0.275 | 9674 260 ²²⁷² | 8399 ¹¹ | 9817 765 ¹²⁷⁹ |
| .226 | 9776 912 ¹⁹¹² | 8898 ¹⁰ | 9875 470 ¹⁰⁷⁷ | .276 | 9671 988 ²²⁷⁸ | 8388 ¹¹ | 9816 486 ¹²⁸⁴ |
| .227 | 9774 991 ¹⁹²¹ | 8888 ¹⁰ | 9874 393 ¹⁰⁸¹ | .277 | 9669 710 ²²⁸⁶ | 8377 ¹¹ | 9815 202 ¹²⁸⁸ |
| .228 | 9773 064 ¹⁹²⁷ | 8879 ¹⁰ | 9873 312 ¹⁰⁸⁶ | .278 | 9667 424 ²²⁹² | 8366 ¹¹ | 9813 914 ¹²⁹² |
| .229 | 9771 129 ¹⁹³⁵ | 8869 ¹⁰ | 9872 226 ¹⁰⁹⁰ | .279 | 9665 132 ²²⁹⁹ | 8355 ¹¹ | 9812 622 ¹²⁹⁶ |
| | | | | | | | |
| 0.230 | 9769 186 | 8860 ¹⁰ | 9871 136 ¹⁰⁹⁴ | 0.280 | 9662 833 ²³⁰⁵ | 8344 ¹¹ | 9811 326 ¹²⁹⁹ |
| .231 | 9767 236 ¹⁹⁵⁰ | 8850 ¹⁰ | 9870 042 ¹⁰⁹⁸ | .281 | 9660 528 ²³¹³ | 8333 ¹¹ | 9810 027 ¹³⁰⁴ |
| .232 | 9765 278 ¹⁹⁵⁸ | 8841 ¹⁰ | 9868 944 ¹¹⁰³ | .282 | 9658 215 ²³¹⁹ | 8322 ¹¹ | 9808 723 ¹³⁰⁸ |
| .233 | 9763 314 ¹⁹⁶⁴ | 8831 ¹⁰ | 9867 841 ¹¹⁰⁷ | .283 | 9655 896 ²³²⁶ | 8310 ¹² | 9807 415 ¹³¹¹ |
| .234 | 9761 341 ¹⁹⁷³ | 8822 ¹⁰ | 9866 734 ¹¹¹¹ | .284 | 9653 570 ²³³³ | 8299 ¹¹ | 9806 104 ¹³¹⁶ |
| | | | | | | | |
| 0.235 | 9759 362 | 8812 ¹⁰ | 9865 623 ¹¹¹⁵ | 0.285 | 9651 237 ²³³⁹ | 8288 ¹¹ | 9804 788 ¹³¹⁹ |
| .236 | 9757 374 ¹⁹⁸⁸ | 8802 ¹⁰ | 9864 508 ¹¹²⁰ | .286 | 9648 898 ²³⁴⁶ | 8277 ¹¹ | 9803 469 ¹³²⁴ |
| .237 | 9755 386 ¹⁹⁹⁴ | 8793 ¹⁰ | 9863 388 ¹¹²⁴ | .287 | 9646 552 ²³⁵³ | 8265 ¹² | 9802 145 ¹³²⁷ |
| .238 | 9753 378 ²⁰⁰² | 8783 ¹⁰ | 9862 264 ¹¹²⁸ | .288 | 9644 199 ²³⁵⁹ | 8254 ¹¹ | 9800 818 ¹³³¹ |
| .239 | 9751 369 ²⁰⁰⁹ | 8773 ¹⁰ | 9861 136 ¹¹³² | .289 | 9641 840 ²³⁶⁶ | 8243 ¹² | 9799 487 ¹³³⁵ |
| | | | | | | | |
| 0.240 | 9749 353 | 8763 ¹⁰ | 9860 004 ¹¹³⁷ | 0.290 | 9639 474 ²³⁷³ | 8231 ¹¹ | 9798 152 ¹³³⁹ |
| .241 | 9747 329 ²⁰²⁴ | 8753 ¹⁰ | 9858 867 ¹¹⁴¹ | .291 | 9637 101 ²³⁷⁹ | 8220 ¹² | 9796 813 ¹³⁴³ |
| .242 | 9745 298 ²⁰³¹ | 8743 ¹⁰ | 9857 726 ¹¹⁴⁵ | .292 | 9634 722 ²³⁸⁶ | 8208 ¹¹ | 9795 470 ¹³⁴⁶ |
| .243 | 9743 259 ²⁰³⁹ | 8734 ⁹ | 9856 581 ¹¹⁴⁹ | .293 | 9632 336 ²³⁹³ | 8197 ¹² | 9794 124 ¹³⁵¹ |
| .244 | 9741 214 ²⁰⁴⁵ | 8724 ¹⁰ | 9855 432 ¹¹⁵³ | .294 | 9629 943 ²³⁹⁹ | 8185 ¹¹ | 9792 773 ¹³⁵⁴ |
| | | | | | | | |
| 0.245 | 9739 161 | 8714 ¹⁰ | 9854 279 ¹¹⁵⁷ | 0.295 | 9627 544 ²⁴⁰⁶ | 8174 ¹² | 9791 419 ¹³⁵⁹ |
| .246 | 9737 101 ²⁰⁶⁰ | 8704 ¹⁰ | 9853 122 ¹¹⁶² | .296 | 9625 138 ²⁴¹² | 8162 ¹¹ | 9790 060 ¹³⁶² |
| .247 | 9735 033 ²⁰⁶⁸ | 8694 ¹⁰ | 9851 960 ¹¹⁶⁶ | .297 | 9622 726 ²⁴¹⁹ | 8151 ¹² | 9788 698 ¹³⁶⁶ |
| .248 | 9732 959 ²⁰⁷⁴ | 8683 ¹¹ | 9850 794 ¹¹⁷⁰ | .298 | 9620 307 ²⁴²⁵ | 8139 ¹² | 9787 332 ¹³⁶⁹ |
| .249 | 9730 877 ²⁰⁸² | 8673 ¹⁰ | 9849 624 ¹¹⁷⁴ | .299 | 9617 882 ²⁴³² | 8127 ¹¹ | 9785 963 ¹³⁷⁴ |
| | | | | | | | |
| 0.250 | 9728 788 | 8663 | 9848 450 | 0.300 | 9615 450 | 8116 | 9784 589 |

TABLE 1.

| $\alpha^{\frac{1}{2}}\mu$ | A | I | N | $\alpha^{\frac{1}{2}}\mu$ | A | I | N |
|---------------------------|--------------------------|--------------------|--------------------------|---------------------------|--------------------------|--------------------|--------------------------|
| 0. | 0. | 2. | 0. | 0. | 0. | 2. | 0. |
| 0.300 | 9615 450 ²⁴³⁰ | 8116 ¹² | 9784 589 ¹³⁷⁷ | 0.350 | 9485 870 ²⁷⁴⁴ | 7498 ¹³ | 9711 184 ¹⁵⁵⁹ |
| .301 | 9613 017 ²⁴⁴⁴ | 8104 ¹² | 9783 212 ¹³⁸² | .351 | 9483 126 ²⁷⁵¹ | 7485 ¹³ | 9709 625 ¹⁵⁶³ |
| .302 | 9610 567 ²⁴⁵² | 8092 ¹¹ | 9781 830 ¹³⁸⁵ | .352 | 9480 375 ²⁷⁵⁶ | 7472 ¹³ | 9708 062 ¹⁵⁶⁶ |
| .303 | 9608 115 ²⁴⁵⁸ | 8081 ¹² | 9780 445 ¹³⁸⁸ | .353 | 9477 619 ²⁷⁶² | 7459 ¹³ | 9706 496 ¹⁵⁷⁰ |
| .304 | 9605 657 ²⁴⁶⁴ | 8069 ¹² | 9779 057 ¹³⁹³ | .354 | 9474 857 ²⁷⁶⁸ | 7446 ¹³ | 9704 926 ¹⁵⁷³ |
| 0.305 | 9603 193 ²⁴⁷⁰ | 8057 ¹² | 9777 664 ¹³⁹⁶ | 0.355 | 9472 089 ²⁷⁷³ | 7433 ¹³ | 9703 353 ¹⁵⁷⁷ |
| .306 | 9600 723 ²⁴⁷⁸ | 8045 ¹² | 9776 268 ¹⁴⁰¹ | .356 | 9469 316 ²⁷⁷⁹ | 7420 ¹³ | 9701 776 ¹⁵⁸⁰ |
| .307 | 9598 245 ²⁴⁸³ | 8033 ¹² | 9774 867 ¹⁴⁰⁴ | .357 | 9466 537 ²⁷⁸⁵ | 7406 ¹³ | 9700 196 ¹⁵⁸⁴ |
| .308 | 9595 762 ²⁴⁹⁰ | 8021 ¹² | 9773 463 ¹⁴⁰⁷ | .358 | 9463 752 ²⁷⁹⁰ | 7393 ¹³ | 9698 612 ¹⁵⁸⁶ |
| .309 | 9593 272 ²⁴⁹⁶ | 8009 ¹¹ | 9772 056 ¹⁴¹² | .359 | 9460 962 ²⁷⁹⁶ | 7380 ¹³ | 9697 026 ¹⁵⁹¹ |
| 0.310 | 9590 776 ²⁵⁰³ | 7998 ¹² | 9770 644 ¹⁴¹⁵ | 0.360 | 9458 166 ²⁸⁰² | 7367 ¹³ | 9695 435 ¹⁵⁹³ |
| .311 | 9588 273 ²⁵⁰⁹ | 7986 ¹² | 9769 229 ¹⁴¹⁹ | .361 | 9455 364 ²⁸⁰⁷ | 7354 ¹³ | 9693 842 ¹⁵⁹⁸ |
| .312 | 9585 764 ²⁵¹⁵ | 7974 ¹² | 9767 810 ¹⁴²³ | .362 | 9452 557 ²⁸¹³ | 7340 ¹³ | 9692 244 ¹⁶⁰⁰ |
| .313 | 9583 249 ²⁵²¹ | 7961 ¹² | 9766 387 ¹⁴²⁶ | .363 | 9449 744 ²⁸¹⁸ | 7327 ¹³ | 9690 644 ¹⁶⁰⁴ |
| .314 | 9580 725 ²⁵²⁸ | 7949 ¹² | 9764 961 ¹⁴³⁰ | .364 | 9446 926 ²⁸²⁴ | 7314 ¹³ | 9689 046 ¹⁶⁰⁷ |
| 0.315 | 9578 200 ²⁵³⁵ | 7937 ¹² | 9763 531 ¹⁴³⁴ | 0.365 | 9444 102 ²⁸²⁹ | 7301 ¹³ | 9687 433 ¹⁶¹¹ |
| .316 | 9575 665 ²⁵⁴⁰ | 7925 ¹² | 9762 097 ¹⁴³⁸ | .366 | 9441 273 ²⁸³⁵ | 7287 ¹³ | 9685 822 ¹⁶¹³ |
| .317 | 9573 125 ²⁵⁴⁷ | 7913 ¹² | 9760 659 ¹⁴⁴¹ | .367 | 9438 438 ²⁸⁴¹ | 7274 ¹³ | 9684 209 ¹⁶¹⁸ |
| .318 | 9570 578 ²⁵⁵³ | 7901 ¹² | 9759 218 ¹⁴⁴⁵ | .368 | 9435 597 ²⁸⁴⁶ | 7260 ¹³ | 9682 591 ¹⁶²⁰ |
| .319 | 9568 025 ²⁵⁵⁹ | 7889 ¹³ | 9757 773 ¹⁴⁴⁹ | .369 | 9432 751 ²⁸⁵¹ | 7247 ¹³ | 9680 971 ¹⁶²⁴ |
| 0.320 | 9565 466 ²⁵⁶⁵ | 7876 ¹² | 9756 324 ¹⁴⁵² | 0.370 | 9429 900 ²⁸⁵⁷ | 7234 ¹³ | 9679 347 ¹⁶²⁷ |
| .321 | 9562 901 ²⁵⁷² | 7864 ¹² | 9754 872 ¹⁴⁵⁶ | .371 | 9427 043 ²⁸⁶² | 7220 ¹³ | 9677 720 ¹⁶³¹ |
| .322 | 9560 323 ²⁵⁷⁷ | 7852 ¹² | 9753 416 ¹⁴⁶⁰ | .372 | 9424 181 ²⁸⁶⁸ | 7207 ¹³ | 9676 089 ¹⁶³⁴ |
| .323 | 9557 752 ²⁵⁸⁴ | 7840 ¹² | 9751 956 ¹⁴⁶³ | .373 | 9421 313 ²⁸⁷³ | 7193 ¹³ | 9674 455 ¹⁶³⁷ |
| .324 | 9555 168 ²⁵⁹⁰ | 7827 ¹² | 9750 493 ¹⁴⁶⁷ | .374 | 9418 440 ²⁸⁷⁹ | 7180 ¹³ | 9672 818 ¹⁶⁴⁰ |
| 0.325 | 9552 578 ²⁵⁹⁷ | 7815 ¹² | 9749 026 ¹⁴⁷¹ | 0.375 | 9415 561 ²⁸⁸⁴ | 7166 ¹³ | 9671 178 ¹⁶⁴⁴ |
| .326 | 9549 981 ²⁶⁰² | 7803 ¹² | 9747 555 ¹⁴⁷⁴ | .376 | 9412 677 ²⁸⁸⁹ | 7153 ¹³ | 9669 534 ¹⁶⁴⁷ |
| .327 | 9547 379 ²⁶⁰⁸ | 7790 ¹² | 9746 081 ¹⁴⁷⁸ | .377 | 9409 788 ²⁸⁹⁴ | 7139 ¹³ | 9667 887 ¹⁶⁵⁰ |
| .328 | 9544 771 ²⁶¹⁵ | 7778 ¹² | 9744 603 ¹⁴⁸² | .378 | 9406 894 ²⁹⁰⁰ | 7126 ¹³ | 9666 237 ¹⁶⁵⁴ |
| .329 | 9542 156 ²⁶²⁰ | 7765 ¹² | 9743 121 ¹⁴⁸⁵ | .379 | 9403 994 ²⁹⁰⁶ | 7112 ¹³ | 9664 583 ¹⁶⁵⁶ |
| 0.330 | 9539 536 ²⁶²⁷ | 7753 ¹² | 9741 636 ¹⁴⁸⁹ | 0.380 | 9401 088 ²⁹¹⁰ | 7098 ¹³ | 9662 927 ¹⁶⁶⁰ |
| .331 | 9536 909 ²⁶³³ | 7740 ¹² | 9740 147 ¹⁴⁹² | .381 | 9398 178 ²⁹¹⁶ | 7085 ¹³ | 9661 267 ¹⁶⁶⁴ |
| .332 | 9534 276 ²⁶³⁸ | 7728 ¹² | 9738 655 ¹⁴⁹⁶ | .382 | 9395 262 ²⁹²² | 7071 ¹³ | 9659 603 ¹⁶⁶⁸ |
| .333 | 9531 638 ²⁶⁴⁵ | 7715 ¹² | 9737 159 ¹⁴⁹⁹ | .383 | 9392 340 ²⁹²⁶ | 7057 ¹³ | 9657 937 ¹⁶⁷⁰ |
| .334 | 9528 993 ²⁶⁵¹ | 7703 ¹² | 9735 660 ¹⁵⁰⁴ | .384 | 9389 414 ²⁹³² | 7043 ¹³ | 9656 267 ¹⁶⁷³ |
| 0.335 | 9526 342 ²⁶⁵⁷ | 7690 ¹² | 9734 156 ¹⁵⁰⁶ | 0.385 | 9386 482 ²⁹³⁷ | 7030 ¹³ | 9654 594 ¹⁶⁷⁶ |
| .336 | 9523 685 ²⁶⁶² | 7677 ¹² | 9732 650 ¹⁵¹¹ | .386 | 9383 545 ²⁹⁴² | 7016 ¹³ | 9652 918 ¹⁶⁷⁹ |
| .337 | 9521 023 ²⁶⁶⁹ | 7665 ¹² | 9731 139 ¹⁵¹³ | .387 | 9380 603 ²⁹⁴⁷ | 7002 ¹³ | 9651 239 ¹⁶⁸³ |
| .338 | 9518 354 ²⁶⁷⁵ | 7652 ¹² | 9729 626 ¹⁵¹⁸ | .388 | 9377 656 ²⁹⁵³ | 6988 ¹³ | 9649 556 ¹⁶⁸⁵ |
| .339 | 9515 679 ²⁶⁸⁰ | 7639 ¹² | 9728 108 ¹⁵²¹ | .389 | 9374 703 ²⁹⁵⁷ | 6975 ¹³ | 9647 871 ¹⁶⁸⁹ |
| 0.340 | 9512 999 ²⁶⁸⁷ | 7627 ¹² | 9726 587 ¹⁵²⁴ | 0.390 | 9371 746 ²⁹⁶³ | 6961 ¹³ | 9646 182 ¹⁶⁹² |
| .341 | 9510 312 ²⁶⁹² | 7614 ¹² | 9725 063 ¹⁵²⁸ | .391 | 9368 783 ²⁹⁶⁸ | 6947 ¹³ | 9644 490 ¹⁶⁹⁵ |
| .342 | 9507 620 ²⁶⁹⁸ | 7601 ¹² | 9723 535 ¹⁵³² | .392 | 9365 815 ²⁹⁷³ | 6933 ¹³ | 9642 795 ¹⁶⁹⁹ |
| .343 | 9504 925 ²⁷⁰⁴ | 7588 ¹² | 9722 003 ¹⁵³⁵ | .393 | 9362 842 ²⁹⁷⁹ | 6919 ¹³ | 9641 096 ¹⁷⁰¹ |
| .344 | 9502 218 ²⁷¹⁰ | 7575 ¹² | 9720 468 ¹⁵³⁸ | .394 | 9359 863 ²⁹⁸³ | 6905 ¹³ | 9639 395 ¹⁷⁰⁵ |
| 0.345 | 9499 508 ²⁷¹⁶ | 7563 ¹² | 9718 930 ¹⁵⁴² | 0.395 | 9356 880 ²⁹⁸⁸ | 6891 ¹³ | 9637 690 ¹⁷⁰⁸ |
| .346 | 9496 792 ²⁷²² | 7550 ¹² | 9717 388 ¹⁵⁴⁶ | .396 | 9353 892 ²⁹⁹⁴ | 6877 ¹³ | 9635 982 ¹⁷¹⁰ |
| .347 | 9494 076 ²⁷²⁷ | 7537 ¹² | 9715 842 ¹⁵⁴⁹ | .397 | 9350 898 ²⁹⁹⁸ | 6863 ¹³ | 9634 272 ¹⁷¹⁴ |
| .348 | 9491 343 ²⁷³⁴ | 7524 ¹² | 9714 293 ¹⁵⁵³ | .398 | 9347 900 ³⁰⁰⁴ | 6849 ¹³ | 9632 558 ¹⁷¹⁸ |
| .349 | 9488 609 ²⁷³⁹ | 7511 ¹² | 9712 740 ¹⁵⁵⁶ | .399 | 9344 896 ³⁰⁰⁸ | 6835 ¹³ | 9630 840 ¹⁷²⁰ |
| 0.350 | 9485 870 | 7498 | 9711 184 | 0.400 | 9341 888 | 6821 | 9629 120 |

TABLE 1.

| $\alpha^1\mu$ | A | I | N | $\alpha^1\mu$ | A | I | N |
|---------------|--------------------------|--------------------|--------------------------|---------------|--------------------------|--------------------|--------------------------|
| | 0. | 2. | 0. | | 0. | 2. | 0. |
| 0.400 | 9341 888 | 6821 | 9629 120 | 0.450 | 9185 403 | 6097 ¹⁵ | 9539 320 |
| .401 | 9338 874 ³⁰¹⁴ | 6807 ¹⁴ | 9627 397 ¹⁷²³ | .451 | 9182 159 ³²⁴⁴ | 6082 ¹⁴ | 9537 451 ¹⁸⁶⁹ |
| .402 | 9335 856 ³⁰¹⁸ | 6793 ¹⁴ | 9625 870 ¹⁷²⁷ | .452 | 9178 911 ³²⁴⁸ | 6068 ¹⁴ | 9535 580 ¹⁸⁷¹ |
| .403 | 9332 832 ³⁰²⁴ | 6779 ¹⁴ | 9623 941 ¹⁷²⁹ | .453 | 9175 658 ³²⁵³ | 6053 ¹⁵ | 9533 706 ¹⁸⁷⁴ |
| .404 | 9329 804 ³⁰²⁸ | 6765 ¹⁴ | 9622 208 ¹⁷³³ | .454 | 9172 402 ³²⁵⁶ | 6038 ¹⁵ | 9531 825 ¹⁸⁷⁷ |
| | | | | | | | 1879 |
| 0.405 | 9326 770 ³⁰³⁸ | 6751 ¹⁴ | 9620 473 ¹⁷³⁹ | 0.455 | 9169 141 ³²⁶⁵ | 6023 ¹⁵ | 9529 950 ¹⁸⁸² |
| .406 | 9323 732 ³⁰⁴³ | 6737 ¹⁵ | 9618 734 ¹⁷⁴² | .456 | 9165 876 ³²⁶⁹ | 6008 ¹⁵ | 9528 068 ¹⁸⁸⁵ |
| .407 | 9320 689 ³⁰⁴⁸ | 6722 ¹⁴ | 9616 992 ¹⁷⁴⁴ | .457 | 9162 607 ³²⁷⁴ | 5993 ¹⁵ | 9526 183 ¹⁸⁸⁷ |
| .408 | 9317 641 ³⁰⁵³ | 6708 ¹⁴ | 9615 248 ¹⁷⁴⁸ | .458 | 9159 333 ³²⁷⁷ | 5978 ¹⁵ | 9524 296 ¹⁸⁹⁰ |
| .409 | 9314 588 ³⁰⁵⁸ | 6694 ¹⁴ | 9613 500 ¹⁷⁵¹ | .459 | 9156 056 ³²⁸² | 5963 ¹⁵ | 9522 406 ¹⁸⁹³ |
| | | | | | | | |
| 0.410 | 9311 530 ³⁰⁶³ | 6680 ¹⁴ | 9611 749 ¹⁷⁵⁴ | 0.460 | 9152 774 ³²⁸⁵ | 5948 ¹⁵ | 9520 513 ¹⁸⁹⁵ |
| .411 | 9308 487 ³⁰⁶⁸ | 6666 ¹⁵ | 9609 995 ¹⁷⁵⁷ | .461 | 9149 489 ³²⁹⁰ | 5933 ¹⁵ | 9518 618 ¹⁸⁹⁸ |
| .412 | 9305 399 ³⁰⁷² | 6651 ¹⁴ | 9608 238 ¹⁷⁶⁰ | .462 | 9146 199 ³²⁹⁴ | 5918 ¹⁵ | 9516 720 ¹⁹⁰⁰ |
| .413 | 9302 327 ³⁰⁷⁷ | 6637 ¹⁴ | 9606 478 ¹⁷⁶² | .463 | 9142 905 ³²⁹⁷ | 5903 ¹⁵ | 9514 820 ¹⁹⁰³ |
| .414 | 9299 250 ³⁰⁸² | 6623 ¹⁵ | 9604 716 ¹⁷⁶⁶ | .464 | 9139 608 ³³⁰² | 5888 ¹⁵ | 9512 917 ¹⁹⁰⁶ |
| | | | | | | | |
| 0.415 | 9296 168 ³⁰⁸⁷ | 6608 ¹⁴ | 9602 950 ¹⁷⁶⁹ | 0.465 | 9136 306 ³³⁰⁶ | 5873 ¹⁵ | 9511 011 ¹⁹⁰⁹ |
| .416 | 9293 081 ³⁰⁹¹ | 6594 ¹⁴ | 9601 181 ¹⁷⁷² | .466 | 9133 000 ³³¹⁰ | 5858 ¹⁵ | 9509 102 ¹⁹¹¹ |
| .417 | 9289 990 ³⁰⁹⁷ | 6580 ¹⁵ | 9599 409 ¹⁷⁷⁵ | .467 | 9129 690 ³³¹³ | 5842 ¹⁵ | 9507 191 ¹⁹¹³ |
| .418 | 9286 893 ³¹⁰⁰ | 6565 ¹⁴ | 9597 634 ¹⁷⁷⁷ | .468 | 9126 377 ³³¹⁸ | 5827 ¹⁵ | 9505 278 ¹⁹¹⁶ |
| .419 | 9283 793 ³¹⁰⁶ | 6551 ¹⁴ | 9595 857 ¹⁷⁸¹ | .469 | 9123 059 ³³²² | 5812 ¹⁵ | 9503 369 ¹⁹¹⁹ |
| | | | | | | | |
| 0.420 | 9280 687 ³¹¹⁰ | 6537 ¹⁵ | 9594 076 ¹⁷⁸⁴ | 0.470 | 9119 737 ³³²⁶ | 5797 ¹⁵ | 9501 443 ¹⁹²¹ |
| .421 | 9277 577 ³¹¹⁵ | 6522 ¹⁴ | 9592 292 ¹⁷⁸⁶ | .471 | 9116 411 ³³²⁹ | 5782 ¹⁵ | 9499 522 ¹⁹²⁴ |
| .422 | 9274 462 ³¹²⁰ | 6508 ¹⁵ | 9590 506 ¹⁷⁹⁰ | .472 | 9113 082 ³³³⁴ | 5767 ¹⁵ | 9497 598 ¹⁹²⁷ |
| .423 | 9271 342 ³¹²⁵ | 6493 ¹⁴ | 9588 716 ¹⁷⁹² | .473 | 9109 748 ³³³⁷ | 5752 ¹⁵ | 9495 671 ¹⁹²⁹ |
| .424 | 9268 217 ³¹²⁸ | 6479 ¹⁵ | 9586 924 ¹⁷⁹⁶ | .474 | 9106 411 ³³⁴¹ | 5736 ¹⁵ | 9493 742 ¹⁹³¹ |
| | | | | | | | |
| 0.425 | 9265 089 ³¹³⁴ | 6464 ¹⁴ | 9585 128 ¹⁷⁹⁸ | 0.475 | 9103 070 ³³⁴⁵ | 5721 ¹⁵ | 9491 811 ¹⁹³⁴ |
| .426 | 9261 955 ³¹³⁸ | 6450 ¹⁵ | 9583 330 ¹⁸⁰¹ | .476 | 9099 725 ³³⁴⁹ | 5706 ¹⁵ | 9489 877 ¹⁹³⁷ |
| .427 | 9258 817 ³¹⁴³ | 6435 ¹⁴ | 9581 529 ¹⁸⁰⁴ | .477 | 9096 376 ³³⁵³ | 5691 ¹⁵ | 9487 940 ¹⁹³⁹ |
| .428 | 9255 674 ³¹⁴⁷ | 6421 ¹⁵ | 9579 725 ¹⁸⁰⁷ | .478 | 9093 023 ³³⁵⁶ | 5676 ¹⁵ | 9486 001 ¹⁹⁴¹ |
| .429 | 9252 527 ³¹⁵² | 6406 ¹⁴ | 9577 918 ¹⁸¹⁰ | .479 | 9089 667 ³³⁶¹ | 5660 ¹⁵ | 9484 060 ¹⁹⁴⁵ |
| | | | | | | | |
| 0.430 | 9249 375 ³¹⁵⁷ | 6392 ¹⁵ | 9576 108 ¹⁸¹² | 0.480 | 9086 306 ³³⁶⁴ | 5645 ¹⁵ | 9482 115 ¹⁹⁴⁶ |
| .431 | 9246 218 ³¹⁶¹ | 6377 ¹⁴ | 9574 296 ¹⁸¹⁶ | .481 | 9082 942 ³³⁶⁸ | 5630 ¹⁵ | 9480 169 ¹⁹⁴⁹ |
| .432 | 9243 057 ³¹⁶⁵ | 6363 ¹⁵ | 9572 480 ¹⁸¹⁸ | .482 | 9079 574 ³³⁷¹ | 5614 ¹⁵ | 9478 220 ¹⁹⁵² |
| .433 | 9239 892 ³¹⁷⁰ | 6348 ¹⁴ | 9570 662 ¹⁸²² | .483 | 9076 203 ³³⁷⁶ | 5599 ¹⁵ | 9476 268 ¹⁹⁵⁴ |
| .434 | 9236 722 ³¹⁷⁵ | 6333 ¹⁵ | 9568 840 ¹⁸²⁴ | .484 | 9072 827 ³³⁷⁹ | 5584 ¹⁵ | 9474 314 ¹⁹⁵⁶ |
| | | | | | | | |
| 0.435 | 9233 547 ³¹⁷⁹ | 6319 ¹⁵ | 9567 016 ¹⁸²⁷ | 0.485 | 9069 448 ³³⁸³ | 5569 ¹⁵ | 9472 358 ¹⁹⁵⁹ |
| .436 | 9230 368 ³¹⁸³ | 6304 ¹⁴ | 9565 189 ¹⁸²⁹ | .486 | 9066 065 ³³⁸⁶ | 5553 ¹⁵ | 9470 399 ¹⁹⁶² |
| .437 | 9227 185 ³¹⁸⁸ | 6289 ¹⁵ | 9563 360 ¹⁸³³ | .487 | 9062 679 ³³⁹¹ | 5538 ¹⁵ | 9468 437 ¹⁹⁶⁴ |
| .438 | 9223 997 ³¹⁹² | 6275 ¹⁴ | 9561 527 ¹⁸³⁵ | .488 | 9059 288 ³³⁹³ | 5523 ¹⁵ | 9466 473 ¹⁹⁶⁶ |
| .439 | 9220 805 ³¹⁹⁷ | 6260 ¹⁵ | 9559 692 ¹⁸³⁸ | .489 | 9055 895 ³³⁹⁸ | 5507 ¹⁵ | 9464 507 ¹⁹⁶⁹ |
| | | | | | | | |
| 0.440 | 9217 608 ³²⁰¹ | 6245 ¹⁴ | 9557 854 ¹⁸⁴¹ | 0.490 | 9052 497 ³⁴⁰¹ | 5492 ¹⁵ | 9462 538 ¹⁹⁷¹ |
| .441 | 9214 407 ³²⁰⁵ | 6231 ¹⁵ | 9556 013 ¹⁸⁴⁴ | .491 | 9049 096 ³⁴⁰⁵ | 5476 ¹⁵ | 9460 567 ¹⁹⁷³ |
| .442 | 9211 202 ³²¹⁰ | 6216 ¹⁴ | 9554 169 ¹⁸⁴⁷ | .492 | 9045 691 ³⁴⁰⁸ | 5461 ¹⁵ | 9458 594 ¹⁹⁷⁶ |
| .443 | 9207 992 ³²¹⁴ | 6201 ¹⁵ | 9552 322 ¹⁸⁴⁹ | .493 | 9042 283 ³⁴¹² | 5446 ¹⁵ | 9456 618 ¹⁹⁷⁹ |
| .444 | 9204 778 ³²¹⁸ | 6186 ¹⁴ | 9550 473 ¹⁸⁵² | .494 | 9038 871 ³⁴¹⁶ | 5430 ¹⁵ | 9454 639 ¹⁹⁸⁰ |
| | | | | | | | |
| 0.445 | 9201 560 ³²²³ | 6172 ¹⁵ | 9548 621 ¹⁸⁵⁵ | 0.495 | 9035 455 ³⁴¹⁹ | 5415 ¹⁵ | 9452 659 ¹⁹⁸⁴ |
| .446 | 9198 337 ³²²⁷ | 6157 ¹⁴ | 9546 766 ¹⁸⁵⁷ | .496 | 9032 036 ³⁴²³ | 5399 ¹⁵ | 9450 675 ¹⁹⁸⁵ |
| .447 | 9195 110 ³²³¹ | 6142 ¹⁵ | 9544 909 ¹⁸⁶¹ | .497 | 9028 613 ³⁴²⁶ | 5384 ¹⁵ | 9448 690 ¹⁹⁸⁸ |
| .448 | 9191 879 ³²³⁶ | 6127 ¹⁴ | 9543 048 ¹⁸⁶³ | .498 | 9025 187 ³⁴³⁰ | 5368 ¹⁵ | 9446 702 ¹⁹⁹⁰ |
| .449 | 9188 643 ³²⁴⁰ | 6112 ¹⁵ | 9541 185 ¹⁸⁶⁵ | .499 | 9021 757 ³⁴³³ | 5353 ¹⁵ | 9444 712 ¹⁹⁹³ |
| | | | | | | | |
| 0.450 | 9185 403 | 6097 | 9539 320 | 0.500 | 9018 324 | 5337 | 9442 719 |

TABLE 1.

| $\alpha^{\frac{1}{2}}\mu$ | A | I | N | $\alpha^{\frac{1}{2}}\mu$ | A | I | N |
|---------------------------|--------------------------|--------------------|--------------------------|---------------------------|--------------------------|--------------------|--------------------------|
| | 0. | 2. | 0. | | 0. | 2. | 0. |
| 0.500 | 9018 324 | 5337 | 9442 719 | 0.550 | 8842 513 | 4552 | 9340 246 |
| .501 | 9014 887 ³⁴⁸⁷ | 5322 ¹⁵ | 9440 724 ¹⁹⁹⁵ | .551 | 8838 920 ³⁵⁹³ | 4536 ¹⁶ | 9338 143 ²¹⁰³ |
| .502 | 9011 447 ³⁴⁴⁰ | 5306 ¹⁶ | 9438 727 ¹⁹⁹⁷ | .552 | 8835 325 ³⁵⁹⁵ | 4520 ¹⁶ | 9336 038 ²¹⁰⁵ |
| .503 | 9008 003 ³⁴⁴⁴ | 5291 ¹⁵ | 9436 727 ²⁰⁰⁰ | .553 | 8831 726 ³⁵⁹⁹ | 4505 ¹⁵ | 9333 931 ²¹⁰⁷ |
| .504 | 9004 556 ³⁴⁴⁷ | 5275 ¹⁶ | 9434 725 ²⁰⁰² | .554 | 8828 125 ³⁶⁰¹ | 4489 ¹⁶ | 9331 822 ²¹⁰⁹ |
| | | 5198 ¹⁵ | 9432 725 ²⁰⁰⁴ | | | | 2111 |
| 0.505 | 9001 108 | 5260 | 9432 721 | 0.555 | 8824 521 | 4473 | 9329 711 |
| .506 | 8997 652 ³⁴⁵⁴ | 5244 ¹⁶ | 9430 714 ²⁰⁰⁷ | .556 | 8820 915 ³⁶⁰⁶ | 4457 ¹⁶ | 9327 598 ²¹¹³ |
| .507 | 8994 194 ³⁴⁵⁸ | 5229 ¹⁵ | 9428 705 ²⁰⁰⁹ | .557 | 8817 305 ³⁶¹⁰ | 4441 ¹⁶ | 9325 483 ²¹¹⁵ |
| .508 | 8990 734 ³⁴⁶⁰ | 5213 ¹⁶ | 9426 694 ²⁰¹¹ | .558 | 8813 693 ³⁶¹² | 4425 ¹⁶ | 9323 366 ²¹¹⁷ |
| .509 | 8987 269 ³⁴⁶⁵ | 5198 ¹⁵ | 9424 681 ²⁰¹³ | .559 | 8810 079 ³⁶¹⁴ | 4409 ¹⁶ | 9321 247 ²¹¹⁹ |
| | | | 2016 | | | | 2121 |
| 0.510 | 8983 802 | 5182 | 9422 665 | 0.560 | 8806 462 | 4393 | 9319 126 |
| .511 | 8980 331 ³⁴⁷¹ | 5167 ¹⁵ | 9420 647 ²⁰¹⁸ | .561 | 8802 842 ³⁶²⁰ | 4377 ¹⁶ | 9317 004 ²¹²² |
| .512 | 8976 857 ³⁴⁷⁴ | 5151 ¹⁶ | 9418 627 ²⁰²⁰ | .562 | 8799 219 ³⁶²³ | 4361 ¹⁶ | 9314 879 ²¹²⁵ |
| .513 | 8973 379 ³⁴⁷⁸ | 5135 ¹⁶ | 9416 604 ²⁰²³ | .563 | 8795 594 ³⁶²⁵ | 4345 ¹⁶ | 9312 753 ²¹²⁶ |
| .514 | 8969 899 ³⁴⁸⁰ | 5120 ¹⁵ | 9414 579 ²⁰²⁵ | .564 | 8791 966 ³⁶²⁸ | 4329 ¹⁶ | 9310 625 ²¹²⁸ |
| | | | 2027 | | | | 2131 |
| 0.515 | 8966 415 | 5104 | 9412 552 | 0.565 | 8788 336 | 4313 | 9308 494 |
| .516 | 8962 927 ³⁴⁸⁸ | 5088 ¹⁶ | 9410 523 ²⁰²⁹ | .566 | 8784 703 ³⁶³³ | 4297 ¹⁶ | 9306 362 ²¹³² |
| .517 | 8959 437 ³⁴⁹⁰ | 5073 ¹⁵ | 9408 491 ²⁰³² | .567 | 8781 068 ³⁶³⁵ | 4281 ¹⁶ | 9304 228 ²¹³⁴ |
| .518 | 8955 943 ³⁴⁹⁴ | 5057 ¹⁶ | 9406 458 ²⁰³³ | .568 | 8777 430 ³⁶³⁸ | 4265 ¹⁶ | 9302 092 ²¹³⁶ |
| .519 | 8952 446 ³⁴⁹⁷ | 5042 ¹⁵ | 9404 422 ²⁰³⁶ | .569 | 8773 789 ³⁶⁴¹ | 4249 ¹⁶ | 9299 955 ²¹³⁷ |
| | | | 2039 | | | | 2140 |
| 0.520 | 8948 946 | 5026 | 9402 383 | 0.570 | 8770 146 | 4233 | 9297 815 |
| .521 | 8945 442 ³⁵⁰⁴ | 5010 ¹⁶ | 9400 343 ²⁰⁴⁰ | .571 | 8766 501 ³⁶⁴⁵ | 4217 ¹⁶ | 9295 674 ²¹⁴¹ |
| .522 | 8941 936 ³⁵⁰⁷ | 4994 ¹⁵ | 9398 300 ²⁰⁴³ | .572 | 8762 853 ³⁶⁴⁸ | 4201 ¹⁶ | 9293 530 ²¹⁴⁴ |
| .523 | 8938 426 ³⁵⁰⁹ | 4979 ¹⁶ | 9396 256 ²⁰⁴⁴ | .573 | 8759 202 ³⁶⁵¹ | 4185 ¹⁶ | 9291 385 ²¹⁴⁵ |
| .524 | 8934 913 ³⁵¹³ | 4963 ¹⁵ | 9394 209 ²⁰⁴⁷ | .574 | 8755 549 ³⁶⁵³ | 4169 ¹⁶ | 9289 238 ²¹⁴⁷ |
| | | | 2049 | | | | 2148 |
| 0.525 | 8931 396 | 4947 | 9392 160 | 0.575 | 8751 894 | 4153 | 9287 090 |
| .526 | 8927 877 ³⁵¹⁹ | 4932 ¹⁵ | 9390 108 ²⁰⁵² | .576 | 8748 236 ³⁶⁵⁸ | 4137 ¹⁶ | 9284 939 ²¹⁵¹ |
| .527 | 8924 356 ³⁵²² | 4916 ¹⁶ | 9388 055 ²⁰⁵³ | .577 | 8744 576 ³⁶⁶⁰ | 4121 ¹⁶ | 9282 787 ²¹⁵² |
| .528 | 8920 829 ³⁵²⁶ | 4900 ¹⁵ | 9385 999 ²⁰⁵⁶ | .578 | 8740 913 ³⁶⁶³ | 4105 ¹⁶ | 9280 632 ²¹⁵⁵ |
| .529 | 8917 307 ³⁵²⁸ | 4884 ¹⁶ | 9383 942 ²⁰⁵⁷ | .579 | 8737 248 ³⁶⁶⁵ | 4089 ¹⁶ | 9278 476 ²¹⁵⁶ |
| | | | 2060 | | | | 2157 |
| 0.530 | 8913 769 | 4869 | 9381 882 | 0.580 | 8733 580 | 4073 | 9276 319 |
| .531 | 8910 234 ³⁵³⁵ | 4853 ¹⁵ | 9379 820 ²⁰⁶² | .581 | 8729 910 ³⁶⁷⁰ | 4057 ¹⁶ | 9274 159 ²¹⁶⁰ |
| .532 | 8906 697 ³⁵³⁷ | 4837 ¹⁶ | 9377 755 ²⁰⁶⁵ | .582 | 8726 238 ³⁶⁷² | 4041 ¹⁶ | 9271 159 ²¹⁶¹ |
| .533 | 8903 156 ³⁵⁴¹ | 4821 ¹⁵ | 9375 689 ²⁰⁶⁶ | .583 | 8722 564 ³⁶⁷⁴ | 4025 ¹⁶ | 9269 835 ²¹⁶³ |
| .534 | 8899 612 ³⁵⁴⁴ | 4806 ¹⁶ | 9373 621 ²⁰⁶⁸ | .584 | 8718 887 ³⁶⁷⁷ | 4009 ¹⁶ | 9267 670 ²¹⁶⁵ |
| | | | 2071 | | | | 2167 |
| 0.535 | 8896 065 | 4790 | 9371 550 | 0.585 | 8715 208 | 3993 | 9265 503 |
| .536 | 8892 516 ³⁵⁴⁹ | 4774 ¹⁵ | 9369 478 ²⁰⁷² | .586 | 8711 526 ³⁶⁸² | 3977 ¹⁶ | 9263 335 ²¹⁶⁸ |
| .537 | 8888 963 ³⁵⁵³ | 4758 ¹⁶ | 9367 403 ²⁰⁷⁵ | .587 | 8707 842 ³⁶⁸⁴ | 3961 ¹⁶ | 9261 165 ²¹⁷⁰ |
| .538 | 8885 407 ³⁵⁵⁶ | 4742 ¹⁵ | 9365 326 ²⁰⁷⁷ | .588 | 8704 156 ³⁶⁸⁶ | 3944 ¹⁶ | 9258 993 ²¹⁷² |
| .539 | 8881 848 ³⁵⁵⁹ | 4727 ¹⁶ | 9363 248 ²⁰⁷⁸ | .589 | 8700 468 ³⁶⁸⁸ | 3928 ¹⁶ | 9256 820 ²¹⁷³ |
| | | | 2081 | | | | 2176 |
| 0.540 | 8878 287 | 4711 | 9361 167 | 0.590 | 8696 777 | 3912 | 9254 644 |
| .541 | 8874 722 ³⁵⁶⁵ | 4695 ¹⁵ | 9359 084 ²⁰⁸³ | .591 | 8693 084 ³⁶⁹³ | 3896 ¹⁶ | 9252 467 ²¹⁷⁷ |
| .542 | 8871 152 ³⁵⁶⁷ | 4679 ¹⁶ | 9356 999 ²⁰⁸⁵ | .592 | 8689 389 ³⁶⁹⁵ | 3880 ¹⁶ | 9250 289 ²¹⁷⁸ |
| .543 | 8867 585 ³⁵⁷⁰ | 4663 ¹⁵ | 9354 912 ²⁰⁸⁷ | .593 | 8685 692 ³⁶⁹⁷ | 3864 ¹⁶ | 9248 108 ²¹⁸¹ |
| .544 | 8864 015 ³⁵⁷³ | 4647 ¹⁶ | 9352 823 ²⁰⁸⁹ | .594 | 8681 993 ³⁶⁹⁹ | 3848 ¹⁶ | 9245 926 ²¹⁸² |
| | | | 2091 | | | | 2183 |
| 0.545 | 8860 436 | 4632 | 9350 732 | 0.595 | 8678 291 | 3832 | 9243 743 |
| .546 | 8856 857 ³⁵⁷⁹ | 4616 ¹⁵ | 9348 639 ²⁰⁹³ | .596 | 8674 587 ³⁷⁰⁴ | 3816 ¹⁶ | 9241 557 ²¹⁸⁶ |
| .547 | 8853 275 ³⁵⁸² | 4600 ¹⁶ | 9346 543 ²⁰⁹⁶ | .597 | 8670 881 ³⁷⁰⁶ | 3800 ¹⁶ | 9239 370 ²¹⁸⁷ |
| .548 | 8849 691 ³⁵⁸⁴ | 4584 ¹⁵ | 9344 446 ²⁰⁹⁷ | .598 | 8667 173 ³⁷⁰⁸ | 3783 ¹⁶ | 9237 181 ²¹⁸⁹ |
| .549 | 8846 103 ³⁵⁸⁸ | 4568 ¹⁶ | 9342 347 ²⁰⁹⁹ | .599 | 8663 463 ³⁷¹⁰ | 3767 ¹⁶ | 9234 991 ²¹⁹⁰ |
| | | | 2101 | | | | 2192 |
| 0.550 | 8842 513 | 4552 | 9340 246 | 0.600 | 8659 750 | 3751 | 9232 799 |

TABLE 2.

| α | c | h | α | c | h |
|----------|----------------------------|------------------------|----------|----------------------------|-----------------------|
| 0.000 | 1.000 0000 ³⁹⁹⁹ | 0.00000 ¹⁰⁰ | 0.050 | 1.019 7631 ³⁹⁰⁵ | 0.04860 ⁹⁵ |
| .001 | .000 3999 ³⁹⁹⁷ | .00100 ¹⁰⁰ | .051 | .020 1536 ³⁹⁰⁴ | .04955 ⁹⁴ |
| .002 | .000 7996 ³⁹⁹⁵ | .00200 ⁹⁹ | .052 | .020 5440 ³⁹⁰² | .05049 ⁹⁴ |
| .003 | .001 1991 ³⁹⁹³ | .00299 ¹⁰⁰ | .053 | .020 9342 ³⁹⁰⁰ | .05143 ⁹⁴ |
| .004 | .001 5984 ³⁹⁹² | .00399 ¹⁰⁰ | .054 | .021 3242 ³⁸⁹⁸ | .05237 ⁹⁴ |
| 0.005 | 1.001 9976 ³⁹⁸⁹ | 0.00499 ⁹⁹ | 0.055 | 1.021 7140 ³⁸⁹⁶ | 0.05331 ⁹⁴ |
| .006 | .002 3965 ³⁹⁸⁸ | .00598 ⁹⁹ | .056 | .022 1036 ³⁸⁹⁵ | .05425 ⁹⁴ |
| .007 | .002 7953 ³⁹⁸⁵ | .00697 ⁹⁹ | .057 | .022 4931 ³⁸⁹³ | .05519 ⁹⁴ |
| .008 | .003 1938 ³⁹⁸⁴ | .00796 ⁹⁹ | .058 | .022 8824 ³⁸⁹¹ | .05613 ⁹³ |
| .009 | .003 5925 ³⁹⁸¹ | .00895 ⁹⁹ | .059 | .023 2715 ³⁸⁸⁹ | .05706 ⁹⁴ |
| 0.010 | 1.003 9903 ³⁹⁸⁰ | 0.00994 ⁹⁹ | 0.060 | 1.023 6604 ³⁸⁸⁸ | 0.05800 ⁹³ |
| .011 | .004 3883 ³⁹⁷⁸ | .01093 ⁹⁹ | .061 | .024 0492 ³⁸⁸⁶ | .05893 ⁹³ |
| .012 | .004 7861 ³⁹⁷⁶ | .01192 ⁹⁹ | .062 | .024 4378 ³⁸⁸⁴ | .05986 ⁹⁴ |
| .013 | .005 1837 ³⁹⁷⁴ | .01290 ⁹⁸ | .063 | .024 8262 ³⁸⁸² | .06080 ⁹³ |
| .014 | .005 5811 ³⁹⁷² | .01389 ⁹⁸ | .064 | .025 2144 ³⁸⁸⁰ | .06173 ⁹³ |
| 0.015 | 1.005 9783 ³⁹⁷⁰ | 0.01487 ⁹⁸ | 0.065 | 1.025 6024 ³⁸⁷⁹ | 0.06266 ⁹³ |
| .016 | .006 3752 ³⁹⁶⁹ | .01585 ⁹⁸ | .066 | .025 9903 ³⁸⁷⁷ | .06359 ⁹² |
| .017 | .006 7722 ³⁹⁶⁶ | .01683 ⁹⁹ | .067 | .026 3780 ³⁸⁷⁵ | .06451 ⁹³ |
| .018 | .007 1688 ³⁹⁶⁵ | .01782 ⁹⁷ | .068 | .026 7655 ³⁸⁷⁴ | .06544 ⁹³ |
| .019 | .007 5653 ³⁹⁶² | .01879 ⁹⁸ | .069 | .027 1529 ³⁸⁷¹ | .06637 ⁹² |
| 0.020 | 1.007 9615 ³⁹⁶¹ | 0.01977 ⁹⁸ | 0.070 | 1.027 5400 ³⁸⁷⁰ | 0.06729 ⁹² |
| .021 | .008 3576 ³⁹⁵⁹ | .02075 ⁹⁷ | .071 | .027 9276 ³⁸⁶⁸ | .06821 ⁹³ |
| .022 | .008 7533 ³⁹⁵⁷ | .02172 ⁹⁸ | .072 | .028 3138 ³⁸⁶⁷ | .06914 ⁹² |
| .023 | .009 1492 ³⁹⁵⁵ | .02270 ⁹⁷ | .073 | .028 7005 ³⁸⁶⁴ | .07006 ⁹² |
| .024 | .009 5447 ³⁹⁵³ | .02367 ⁹⁷ | .074 | .029 0869 ³⁸⁶³ | .07098 ⁹² |
| 0.025 | 1.009 9400 ³⁹⁵² | 0.02464 ⁹⁸ | 0.075 | 1.029 4732 ³⁸⁶¹ | 0.07190 ⁹² |
| .026 | .010 3352 ³⁹⁴⁹ | .02562 ⁹⁷ | .076 | .029 8593 ³⁸⁶⁰ | .07282 ⁹¹ |
| .027 | .010 7301 ³⁹⁴⁸ | .02659 ⁹⁷ | .077 | .030 2453 ³⁸⁵⁷ | .07373 ⁹² |
| .028 | .011 1249 ³⁹⁴⁶ | .02756 ⁹⁶ | .078 | .030 6310 ³⁸⁵⁶ | .07465 ⁹² |
| .029 | .011 5195 ³⁹⁴⁴ | .02852 ⁹⁷ | .079 | .031 0166 ³⁸⁵⁵ | .07557 ⁹¹ |
| 0.030 | 1.011 9139 ³⁹⁴² | 0.02949 ⁹⁷ | 0.080 | 1.031 4021 ³⁸⁵² | 0.07648 ⁹¹ |
| .031 | .012 3081 ³⁹⁴⁰ | .03046 ⁹⁶ | .081 | .031 7873 ³⁸⁵¹ | .07739 ⁹² |
| .032 | .012 7021 ³⁹³⁸ | .03142 ⁹⁷ | .082 | .032 1724 ³⁸⁴⁹ | .07831 ⁹¹ |
| .033 | .013 0959 ³⁹³⁷ | .03238 ⁹⁶ | .083 | .032 5573 ³⁸⁴⁷ | .07922 ⁹¹ |
| .034 | .013 4896 ³⁹³⁴ | .03335 ⁹⁶ | .084 | .032 9420 ³⁸⁴⁶ | .08013 ⁹¹ |
| 0.035 | 1.013 8830 ³⁹³³ | 0.03431 ⁹⁶ | 0.085 | 1.033 3266 ³⁸⁴⁴ | 0.08104 ⁹¹ |
| .036 | .014 2763 ³⁹³¹ | .03527 ⁹⁶ | .086 | .033 7116 ³⁸⁴² | .08195 ⁹⁰ |
| .037 | .014 6694 ³⁹²⁹ | .03623 ⁹⁶ | .087 | .034 0952 ³⁸⁴⁰ | .08285 ⁹¹ |
| .038 | .015 0623 ³⁹²⁸ | .03719 ⁹⁵ | .088 | .034 4792 ³⁸³⁹ | .08376 ⁹¹ |
| .039 | .015 4551 ³⁹²⁵ | .03814 ⁹⁶ | .089 | .034 8631 ³⁸³⁷ | .08467 ⁹⁰ |
| 0.040 | 1.015 8476 ³⁹²⁴ | 0.03910 ⁹⁵ | 0.090 | 1.035 2468 ³⁸³⁵ | 0.08557 ⁹⁰ |
| .041 | .016 2400 ³⁹²² | .04005 ⁹⁶ | .091 | .035 6303 ³⁸³⁴ | .08647 ⁹¹ |
| .042 | .016 6322 ³⁹²⁰ | .04101 ⁹⁵ | .092 | .036 0137 ³⁸³² | .08738 ⁹¹ |
| .043 | .017 0242 ³⁹¹⁸ | .04196 ⁹⁵ | .093 | .036 3969 ³⁸³⁰ | .08828 ⁹⁰ |
| .044 | .017 4160 ³⁹¹⁶ | .04291 ⁹⁵ | .094 | .036 7799 ³⁸²⁸ | .08918 ⁹⁰ |
| 0.045 | 1.017 8076 ³⁹¹⁵ | 0.04386 ⁹⁵ | 0.095 | 1.037 1627 ³⁸²⁷ | 0.09008 ⁸⁹ |
| .046 | .018 1991 ³⁹¹² | .04481 ⁹⁵ | .096 | .037 5454 ³⁸²⁵ | .09097 ⁹⁰ |
| .047 | .018 5903 ³⁹¹¹ | .04576 ⁹⁵ | .097 | .037 9279 ³⁸²⁴ | .09187 ⁹⁰ |
| .048 | .018 9814 ³⁹⁰⁹ | .04671 ⁹⁵ | .098 | .038 3103 ³⁸²¹ | .09277 ⁹⁰ |
| .049 | .019 3723 ³⁹⁰⁸ | .04766 ⁹⁴ | .099 | .038 6924 ³⁸²¹ | .09366 ⁸⁹ |
| 0.050 | 1.019 7631 | 0.04860 | 0.100 | 1.039 0745 | 0.09456 |

TABLE 3.

| $\alpha^{\frac{1}{2}}\sigma$ | J | K | $\alpha^{\frac{1}{2}}\sigma$ | J | K |
|------------------------------|------------|--------------------------------|------------------------------|--------------------------|--------------------------------|
| 0.000 | 1.000 0000 | 0.000 0000 | 0.050 | 1.000 3750 | 0.000 0072 |
| .001 | .000 0002 | 0000 ⁰ | .051 | .000 3902 ¹⁵² | 0074 ² |
| .002 | .000 0006 | 0000 ⁰ | .052 | .000 4056 ¹⁵⁴ | 0077 ³ |
| .003 | .000 0014 | 0000 ⁰ | .053 | .000 4214 ¹⁵⁸ | 0080 ³ |
| .004 | .000 0024 | 0000 ⁰ ₁ | .054 | .000 4374 ¹⁶⁰ | 0083 ⁴ |
| 0.005 | 1.000 0038 | 0.000 0001 | 0.055 | 1.000 4538 | 0.000 0087 |
| .006 | .000 0054 | 0001 ⁰ | .056 | .000 4704 ¹⁶⁶ | 0090 ³ |
| .007 | .000 0074 | 0001 ⁰ | .057 | .000 4874 ¹⁷⁰ | 0093 ³ |
| .008 | .000 0096 | 0002 ¹ | .058 | .000 5046 ¹⁷² | 0096 ³ |
| .009 | .000 0122 | 0002 ⁰ ₁ | .059 | .000 5222 ¹⁷⁶ | 0100 ⁴ ₃ |
| 0.010 | 1.000 0150 | 0.000 0003 | 0.060 | 1.000 5400 | 0.000 0103 |
| .011 | .000 0182 | 0003 ⁰ | .061 | .000 5582 ¹⁸² | 0106 ³ |
| .012 | .000 0216 | 0004 ¹ | .062 | .000 5766 ¹⁸⁴ | 0110 ⁴ |
| .013 | .000 0254 | 0005 ¹ | .063 | .000 5954 ¹⁸⁸ | 0114 ⁴ |
| .014 | .000 0294 | 0006 ⁰ ₁ | .064 | .000 6144 ¹⁹⁰ | 0117 ⁴ ₃ |
| 0.015 | 1.000 0338 | 0.000 0006 | 0.065 | 1.000 6338 | 0.000 0121 |
| .016 | .000 0384 | 0007 ¹ | .066 | .000 6534 ¹⁹⁶ | 0125 ⁴ |
| .017 | .000 0434 | 0008 ¹ | .067 | .000 6734 ²⁰⁰ | 0128 ³ |
| .018 | .000 0486 | 0009 ¹ | .068 | .000 6936 ²⁰² | 0132 ⁴ |
| .019 | .000 0542 | 0010 ¹ ₁ | .069 | .000 7142 ²⁰⁶ | 0136 ⁴ ₃ |
| 0.020 | 1.000 0600 | 0.000 0011 | 0.070 | 1.000 7350 | 0.000 0140 |
| .021 | .000 0662 | 0013 ² | .071 | .000 7562 ²¹² | 0144 ⁴ |
| .022 | .000 0726 | 0014 ¹ | .072 | .000 7776 ²¹⁴ | 0148 ⁴ |
| .023 | .000 0794 | 0015 ¹ | .073 | .000 7994 ²¹⁸ | 0153 ⁵ |
| .024 | .000 0864 | 0016 ² | .074 | .000 8214 ²²⁰ | 0157 ⁴ ₃ |
| 0.025 | 1.000 0938 | 0.000 0018 | 0.075 | 1.000 8438 | 0.000 0161 |
| .026 | .000 1014 | 0019 ¹ | .076 | .000 8664 ²²⁶ | 0165 ⁴ |
| .027 | .000 1094 | 0021 ² | .077 | .000 8894 ²³⁰ | 0170 ⁵ |
| .028 | .000 1176 | 0022 ¹ | .078 | .000 9126 ²³² | 0174 ⁴ |
| .029 | .000 1262 | 0024 ² ₂ | .079 | .000 9362 ²³⁶ | 0179 ⁵ ₄ |
| 0.030 | 1.000 1350 | 0.000 0026 | 0.080 | 1.000 9600 | 0.000 0183 |
| .031 | .000 1442 | 0027 ¹ | .081 | .000 9842 ²⁴² | 0188 ⁵ |
| .032 | .000 1536 | 0029 ² | .082 | .001 0086 ²⁴⁴ | 0193 ⁵ |
| .033 | .000 1634 | 0031 ² | .083 | .001 0334 ²⁴⁸ | 0197 ⁴ |
| .034 | .000 1734 | 0033 ² ₂ | .084 | .001 0584 ²⁵⁰ | 0202 ⁵ ₅ |
| 0.035 | 1.000 1838 | 0.000 0035 | 0.085 | 1.001 0838 | 0.000 0207 |
| .036 | .000 1944 | 0037 ² | .086 | .001 1094 ²⁵⁶ | 0212 ⁵ |
| .037 | .000 2054 | 0039 ² | .087 | .001 1354 ²⁶⁰ | 0217 ⁵ |
| .038 | .000 2166 | 0041 ² | .088 | .001 1616 ²⁶² | 0222 ⁵ |
| .039 | .000 2282 | 0043 ³ ₃ | .089 | .001 1882 ²⁶⁶ | 0227 ⁵ ₅ |
| 0.040 | 1.000 2400 | 0.000 0046 | 0.090 | 1.001 2150 | 0.000 0232 |
| .041 | .000 2522 | 0048 ² | .091 | .001 2422 ²⁷² | 0237 ⁵ |
| .042 | .000 2646 | 0050 ² | .092 | .001 2697 ²⁷⁵ | 0243 ⁶ |
| .043 | .000 2774 | 0053 ³ | .093 | .001 2974 ²⁷⁷ | 0248 ⁶ |
| .044 | .000 2904 | 0055 ³ ₃ | .094 | .001 3255 ²⁸¹ | 0253 ⁵ ₆ |
| 0.045 | 1.000 3038 | 0.000 0058 | 0.095 | 1.001 3538 | 0.000 0259 |
| .046 | .000 3174 | 0061 ³ | .096 | .001 3825 ²⁸⁷ | 0264 ⁵ |
| .047 | .000 3314 | 0063 ² | .097 | .001 4114 ²⁸⁹ | 0270 ⁶ |
| .048 | .000 3456 | 0066 ³ | .098 | .001 4407 ²⁹³ | 0275 ⁵ |
| .049 | .000 3602 | 0069 ³ ₃ | .099 | .001 4702 ²⁹⁵ | 0281 ⁶ ₆ |
| 0.050 | 1.000 3750 | 0.000 0072 | 0.100 | 1.001 5001 | 0.000 0287 |

TABLE 3.

| $\alpha^1\sigma$ | J | K | $\alpha^1\sigma$ | J | K |
|------------------|--------------------------|-------------------|------------------|--------------------------|--------------------|
| 0.100 | 1.001 5001 | 0.000 0287 | 0.150 | 1.003 3754 | 0.000 0649 |
| .101 | .001 5302 ³⁰¹ | 0293 ⁶ | .151 | .003 4205 ⁴⁵¹ | 0657 ⁸ |
| .102 | .001 5607 ³⁰⁵ | 0298 ⁶ | .152 | .003 4660 ⁴⁵⁵ | 0666 ⁹ |
| .103 | .001 5914 ³⁰⁷ | 0304 ⁶ | .153 | .003 5117 ⁴⁵⁷ | 0675 ⁹ |
| .104 | .001 6225 ³¹¹ | 0310 ⁶ | .154 | .003 5578 ⁴⁶¹ | 0684 ⁹ |
| | | | | | |
| 0.105 | 1.001 6538 | 0.000 0316 | 0.155 | 1.003 6042 | 0.000 0693 |
| .106 | .001 6855 ³¹⁷ | 0322 ⁶ | .156 | .003 6508 ⁴⁶⁶ | 0702 ⁹ |
| .107 | .001 7174 ³¹⁹ | 0329 ⁷ | .157 | .003 6978 ⁴⁷⁰ | 0711 ⁹ |
| .108 | .001 7497 ³²³ | 0335 ⁶ | .158 | .003 7450 ⁴⁷² | 0720 ⁹ |
| .109 | .001 7822 ³²⁵ | 0341 ⁶ | .159 | .003 7926 ⁴⁷⁶ | 0730 ¹⁰ |
| | | | | | |
| 0.110 | 1.001 8151 | 0.000 0347 | 0.160 | 1.003 8405 | 0.000 0739 |
| .111 | .001 8483 ³³² | 0354 ⁷ | .161 | .003 8886 ⁴⁸¹ | 0748 ⁹ |
| .112 | .001 8817 ³³⁴ | 0360 ⁶ | .162 | .003 9371 ⁴⁸⁵ | 0758 ¹⁰ |
| .113 | .001 9155 ³³⁸ | 0367 ⁷ | .163 | .003 9859 ⁴⁸⁸ | 0767 ⁹ |
| .114 | .001 9495 ³⁴⁰ | 0373 ⁶ | .164 | .004 0349 ⁴⁹⁰ | 0777 ¹⁰ |
| | | | | | |
| 0.115 | 1.001 9839 | 0.000 0380 | 0.165 | 1.004 0843 | 0.000 0786 |
| .116 | .002 0185 ³⁴⁶ | 0386 ⁶ | .166 | .004 1339 ⁴⁹⁶ | 0796 ¹⁰ |
| .117 | .002 0535 ³⁵⁰ | 0393 ⁷ | .167 | .004 1839 ⁵⁰⁰ | 0806 ¹⁰ |
| .118 | .002 0887 ³⁵² | 0400 ⁷ | .168 | .004 2342 ⁵⁰³ | 0815 ⁹ |
| .119 | .002 1243 ³⁵⁶ | 0407 ⁷ | .169 | .004 2847 ⁵⁰⁵ | 0825 ¹⁰ |
| | | | | | |
| 0.120 | 1.002 1601 | 0.000 0414 | 0.170 | 1.004 3356 | 0.000 0835 |
| .121 | .002 1963 ³⁶² | 0421 ⁷ | .171 | .004 3868 ⁵¹² | 0845 ¹⁰ |
| .122 | .002 2328 ³⁶⁵ | 0428 ⁷ | .172 | .004 4382 ⁵¹⁴ | 0855 ¹⁰ |
| .123 | .002 2695 ³⁶⁷ | 0435 ⁷ | .173 | .004 4900 ⁵¹⁸ | 0865 ¹⁰ |
| .124 | .002 3066 ³⁷¹ | 0442 ⁷ | .174 | .004 5421 ⁵²¹ | 0875 ¹⁰ |
| | | | | | |
| 0.125 | 1.002 3439 | 0.000 0449 | 0.175 | 1.004 5944 | 0.000 0886 |
| .126 | .002 3816 ³⁷⁷ | 0456 ⁷ | .176 | .004 6471 ⁵²⁷ | 0896 ¹⁰ |
| .127 | .002 4195 ³⁷⁹ | 0464 ⁸ | .177 | .004 7000 ⁵²⁹ | 0906 ¹⁰ |
| .128 | .002 4578 ³⁸³ | 0471 ⁷ | .178 | .004 7533 ⁵³³ | 0917 ¹¹ |
| .129 | .002 4963 ³⁸⁵ | 0479 ⁸ | .179 | .004 8069 ⁵³⁶ | 0927 ¹⁰ |
| | | | | | |
| 0.130 | 1.002 5352 | 0.000 0486 | 0.180 | 1.004 8607 | 0.000 0938 |
| .131 | .002 5744 ³⁹² | 0494 ⁸ | .181 | .004 9149 ⁵⁴² | 0948 ¹⁰ |
| .132 | .002 6138 ³⁹⁴ | 0501 ⁷ | .182 | .004 9694 ⁵⁴⁵ | 0959 ¹¹ |
| .133 | .002 6536 ³⁹⁸ | 0509 ⁸ | .183 | .005 0242 ⁵⁴⁸ | 0969 ¹⁰ |
| .134 | .002 6936 ⁴⁰⁰ | 0517 ⁸ | .184 | .005 0792 ⁵⁵⁰ | 0980 ¹¹ |
| | | | | | |
| 0.135 | 1.002 7340 | 0.000 0524 | 0.185 | 1.005 1346 | 0.000 0991 |
| .136 | .002 7746 ⁴⁰⁶ | 0532 ⁸ | .186 | .005 1903 ⁵⁵⁷ | 1002 ¹¹ |
| .137 | .002 8156 ⁴¹⁰ | 0540 ⁸ | .187 | .005 2462 ⁵⁵⁹ | 1013 ¹¹ |
| .138 | .002 8569 ⁴¹³ | 0548 ⁸ | .188 | .005 3025 ⁵⁶³ | 1024 ¹¹ |
| .139 | .002 8984 ⁴¹⁵ | 0556 ⁸ | .189 | .005 3591 ⁵⁶⁶ | 1035 ¹¹ |
| | | | | | |
| 0.140 | 1.002 9403 | 0.000 0564 | 0.190 | 1.005 4159 | 0.000 1046 |
| .141 | .002 9824 ⁴²¹ | 0572 ⁸ | .191 | .005 4731 ⁵⁷² | 1057 ¹¹ |
| .142 | .003 0249 ⁴²⁵ | 0581 ⁹ | .192 | .005 5306 ⁵⁷⁵ | 1069 ¹² |
| .143 | .003 0676 ⁴²⁷ | 0589 ⁸ | .193 | .005 5883 ⁵⁷⁷ | 1080 ¹¹ |
| .144 | .003 1107 ⁴³¹ | 0597 ⁸ | .194 | .005 6464 ⁵⁸¹ | 1091 ¹¹ |
| | | | | | |
| 0.145 | 1.003 1541 | 0.000 0606 | 0.195 | 1.005 7048 | 0.000 1103 |
| .146 | .003 1977 ⁴³⁶ | 0614 ⁸ | .196 | .005 7635 ⁵⁸⁷ | 1114 ¹² |
| .147 | .003 2417 ⁴⁴⁰ | 0623 ⁹ | .197 | .005 8224 ⁵⁸⁹ | 1126 ¹² |
| .148 | .003 2859 ⁴⁴² | 0631 ⁸ | .198 | .005 8817 ⁵⁹³ | 1137 ¹¹ |
| .149 | .003 3305 ⁴⁴⁶ | 0640 ⁹ | .199 | .005 9413 ⁵⁹⁶ | 1149 ¹² |
| | | | | | |
| 0.150 | 1.003 3754 | 0.000 0649 | 0.200 | 1.006 0011 | 0.000 1161 |

TABLE 3.

| $\alpha^{\frac{1}{2}}\sigma$ | J | K | $\alpha^{\frac{1}{2}}\sigma$ | J | K |
|------------------------------|---------------------------|--------------------------|------------------------------|---------------------------|--------------------------|
| 0.200 | 1.006 0011 ⁸⁰² | 0.000 1161 ¹² | 0.250 | 1.009 3778 ⁷⁶² | 0.000 1830 ¹⁵ |
| .201 | .006 0613 ⁸⁰⁵ | 1173 ¹² | .251 | .009 4530 ⁷⁵⁵ | 1845 ¹⁵ |
| .202 | .006 1218 ⁸⁰⁸ | 1185 ¹¹ | .252 | .009 5285 ⁷⁵⁸ | 1860 ¹⁵ |
| .203 | .006 1826 ⁸¹⁰ | 1196 ¹³ | .253 | .009 6043 ⁷⁶¹ | 1875 ¹⁵ |
| .204 | .006 2436 ⁸¹⁴ | 1209 ¹² | .254 | .009 6804 ⁷⁶⁴ | 1890 ¹⁵ |
| 0.205 | 1.006 3050 ⁸¹⁷ | 0.000 1221 ¹² | 0.255 | 1.009 7568 ⁷⁶⁷ | 0.000 1905 ¹⁶ |
| .206 | .006 3667 ⁸²⁰ | 1233 ¹² | .256 | .009 8335 ⁷⁷⁰ | 1921 ¹⁶ |
| .207 | .006 4287 ⁸²² | 1245 ¹² | .257 | .009 9105 ⁷⁷³ | 1936 ¹⁶ |
| .208 | .006 4909 ⁸²⁶ | 1257 ¹² | .258 | .009 9878 ⁷⁷⁶ | 1952 ¹⁶ |
| .209 | .006 5535 ⁸²⁹ | 1269 ¹³ | .259 | .010 0654 ⁷⁷⁹ | 1967 ¹⁶ |
| 0.210 | 1.006 6164 ⁸³² | 0.000 1282 ¹² | 0.260 | 1.010 1433 ⁷⁸² | 0.000 1983 ¹⁵ |
| .211 | .006 6796 ⁸³⁴ | 1294 ¹³ | .261 | .010 2215 ⁷⁸⁵ | 1998 ¹⁶ |
| .212 | .006 7430 ⁸³⁸ | 1307 ¹² | .262 | .010 3000 ⁷⁸⁸ | 2014 ¹⁶ |
| .213 | .006 8068 ⁸⁴¹ | 1319 ¹³ | .263 | .010 3788 ⁷⁹¹ | 2030 ¹⁶ |
| .214 | .006 8709 ⁸⁴⁴ | 1332 ¹³ | .264 | .010 4579 ⁷⁹⁴ | 2046 ¹⁶ |
| 0.215 | 1.006 9353 ⁸⁴⁷ | 0.000 1345 ¹³ | 0.265 | 1.010 5373 ⁷⁹⁷ | 0.000 2062 ¹⁶ |
| .216 | .007 0000 ⁸⁴⁹ | 1358 ¹² | .266 | .010 6170 ⁸⁰⁰ | 2078 ¹⁶ |
| .217 | .007 0649 ⁸⁵³ | 1370 ¹³ | .267 | .010 6970 ⁸⁰³ | 2094 ¹⁶ |
| .218 | .007 1302 ⁸⁵⁶ | 1383 ¹³ | .268 | .010 7773 ⁸⁰⁶ | 2110 ¹⁶ |
| .219 | .007 1958 ⁸⁵⁹ | 1396 ¹³ | .269 | .010 8579 ⁸⁰⁹ | 2126 ¹⁶ |
| 0.220 | 1.007 2617 ⁸⁶¹ | 0.000 1409 ¹³ | 0.270 | 1.010 9388 ⁸¹² | 0.000 2143 ¹⁶ |
| .221 | .007 3278 ⁸⁶⁵ | 1422 ¹³ | .271 | .011 0200 ⁸¹⁵ | 2159 ¹⁶ |
| .222 | .007 3943 ⁸⁶⁸ | 1435 ¹⁴ | .272 | .011 1015 ⁸¹⁸ | 2175 ¹⁶ |
| .223 | .007 4611 ⁸⁷¹ | 1449 ¹³ | .273 | .011 1833 ⁸²¹ | 2192 ¹⁶ |
| .224 | .007 5282 ⁸⁷⁴ | 1462 ¹³ | .274 | .011 2654 ⁸²⁴ | 2208 ¹⁶ |
| 0.225 | 1.007 5956 ⁸⁷⁷ | 0.000 1475 ¹⁴ | 0.275 | 1.011 3478 ⁸²⁷ | 0.000 2225 ¹⁷ |
| .226 | .007 6633 ⁸⁷⁹ | 1489 ¹³ | .276 | .011 4305 ⁸³⁰ | 2242 ¹⁷ |
| .227 | .007 7312 ⁸⁸³ | 1502 ¹⁴ | .277 | .011 5135 ⁸³³ | 2258 ¹⁶ |
| .228 | .007 7995 ⁸⁸⁶ | 1516 ¹³ | .278 | .011 5968 ⁸³⁷ | 2275 ¹⁷ |
| .229 | .007 8681 ⁸⁸⁹ | 1529 ¹⁴ | .079 | .011 6805 ⁸³⁹ | 2292 ¹⁷ |
| 0.230 | 1.007 9370 ⁸⁹² | 0.000 1543 ¹⁴ | 0.280 | 1.011 7644 ⁸⁴² | 0.000 2309 ¹⁷ |
| .231 | .008 0062 ⁸⁹⁵ | 1557 ¹³ | .281 | .011 8486 ⁸⁴⁵ | 2326 ¹⁷ |
| .232 | .008 0757 ⁸⁹⁷ | 1570 ¹⁴ | .282 | .011 9331 ⁸⁴⁸ | 2343 ¹⁷ |
| .233 | .008 1454 ⁷⁰¹ | 1584 ¹⁴ | .283 | .012 0179 ⁸⁵¹ | 2360 ¹⁸ |
| .234 | .008 2155 ⁷⁰⁴ | 1598 ¹⁴ | .284 | .012 1030 ⁸⁵⁴ | 2378 ¹⁷ |
| 0.235 | 1.008 2859 ⁷⁰⁷ | 0.000 1612 ¹⁴ | 0.285 | 1.012 1884 ⁸⁵⁸ | 0.000 2395 ¹⁷ |
| .236 | .008 3566 ⁷¹⁰ | 1626 ¹⁴ | .286 | .012 2742 ⁸⁶⁰ | 2412 ¹⁸ |
| .237 | .008 4276 ⁷¹³ | 1640 ¹⁵ | .287 | .012 3602 ⁸⁶³ | 2430 ¹⁷ |
| .238 | .008 4989 ⁷¹⁶ | 1654 ¹⁵ | .288 | .012 4465 ⁸⁶⁶ | 2447 ¹⁸ |
| .239 | .008 5705 ⁷¹⁹ | 1669 ¹⁴ | .289 | .012 5331 ⁸⁶⁹ | 2465 ¹⁷ |
| 0.240 | 1.008 6424 ⁷²² | 0.000 1683 ¹⁴ | 0.290 | 1.012 6200 ⁸⁷² | 0.000 2482 ¹⁸ |
| .241 | .008 7146 ⁷²⁴ | 1697 ¹⁵ | .291 | .012 7072 ⁸⁷⁶ | 2500 ¹⁸ |
| .242 | .008 7870 ⁷²⁸ | 1712 ¹⁴ | .292 | .012 7948 ⁸⁷⁸ | 2518 ¹⁸ |
| .243 | .008 8598 ⁷³¹ | 1726 ¹⁵ | .293 | .012 8826 ⁸⁸¹ | 2536 ¹⁷ |
| .244 | .008 9329 ⁷³⁴ | 1741 ¹⁴ | .294 | .012 9707 ⁸⁸⁴ | 2553 ¹⁸ |
| 0.245 | 1.009 0063 ⁷³⁷ | 0.000 1755 ¹⁵ | 0.295 | 1.013 0591 ⁸⁸⁸ | 0.000 2571 ¹⁸ |
| .246 | .009 0800 ⁷⁴⁰ | 1770 ¹⁵ | .296 | .013 1479 ⁸⁹⁰ | 2589 ¹⁹ |
| .247 | .009 1540 ⁷⁴³ | 1785 ¹⁵ | .297 | .013 2369 ⁸⁹³ | 2608 ¹⁸ |
| .248 | .009 2283 ⁷⁴⁶ | 1800 ¹⁵ | .298 | .013 3262 ⁸⁹⁶ | 2626 ¹⁸ |
| .249 | .009 3029 ⁷⁴⁹ | 1815 ¹⁵ | .299 | .013 4158 ⁹⁰⁰ | 2644 ¹⁸ |
| 0.250 | 1.009 3778 | 0.000 1830 | 0.300 | 1.013 5058 | 0.000 2662 |

TABLE 3.

| $\alpha^{\circ}\sigma$ | J | K | $\alpha^{\circ}\sigma$ | J | K |
|------------------------|---------------------------|--------------------|------------------------|---------------------------|--------------------|
| 0.300 | 1.013 5058 | 0.000 2662 | 0.350 | 1.018 3856 | 0.000 3668 |
| .301 | .013 5960 ⁹⁰² | 2681 ¹⁹ | .351 | .018 4909 ¹⁰⁵³ | 3690 ²² |
| .302 | .013 6865 ⁹⁰⁵ | 2699 ¹⁸ | .352 | .018 5965 ¹⁰⁵⁶ | 3712 ²² |
| .303 | .013 7773 ⁹⁰⁸ | 2718 ¹⁸ | .353 | .018 7024 ¹⁰⁵⁹ | 3734 ²² |
| .304 | .013 8685 ⁹¹² | 2736 ¹⁸ | .354 | .018 8085 ¹⁰⁶¹ | 3756 ²² |
| | | 914 ¹⁹ | | | 1085 ²³ |
| 0.305 | 1.013 9599 | 0.000 2755 | 0.355 | 1.018 9150 | 0.000 3779 |
| .306 | .014 0516 ⁹¹⁷ | 2774 ¹⁹ | .356 | .019 0218 ¹⁰⁶⁸ | 3801 ²² |
| .307 | .014 1437 ⁹²¹ | 2793 ¹⁹ | .357 | .019 1289 ¹⁰⁷¹ | 3823 ²² |
| .308 | .014 2360 ⁹²³ | 2811 ¹⁸ | .358 | .019 2362 ¹⁰⁷³ | 3846 ²³ |
| .309 | .014 3280 ⁹²⁶ | 2830 ¹⁹ | .359 | .019 3439 ¹⁰⁷⁷ | 3868 ²² |
| | | 930 ¹⁹ | | | 1080 ²³ |
| 0.310 | 1.014 4216 | 0.000 2849 | 0.360 | 1.019 4519 | 0.000 3891 |
| .311 | .014 5148 ⁹³² | 2868 ¹⁹ | .361 | .019 5602 ¹⁰⁸³ | 3914 ²³ |
| .312 | .014 6083 ⁹³⁵ | 2888 ²⁰ | .362 | .019 6688 ¹⁰⁸⁶ | 3936 ²² |
| .313 | .014 7022 ⁹³⁹ | 2907 ¹⁹ | .363 | .019 7777 ¹⁰⁸⁹ | 3959 ²³ |
| .314 | .014 7963 ⁹⁴¹ | 2926 ¹⁹ | .364 | .019 8868 ¹⁰⁹¹ | 3982 ²³ |
| | | 944 ¹⁹ | | | 1095 ²³ |
| 0.315 | 1.014 8907 | 0.000 2945 | 0.365 | 1.019 9963 | 0.000 4005 |
| .316 | .014 9855 ⁹⁴⁸ | 2965 ²⁰ | .366 | .020 1061 ¹⁰⁹⁸ | 4028 ²³ |
| .317 | .015 0805 ⁹⁵⁰ | 2984 ¹⁹ | .367 | .020 2162 ¹¹⁰¹ | 4051 ²³ |
| .318 | .015 1759 ⁹⁵⁴ | 3004 ²⁰ | .368 | .020 3266 ¹¹⁰⁴ | 4075 ²⁴ |
| .319 | .015 2715 ⁹⁵⁶ | 3024 ¹⁹ | .369 | .020 4373 ¹¹⁰⁷ | 4098 ²³ |
| | | 959 ¹⁹ | | | 1110 ²³ |
| 0.320 | 1.015 3674 | 0.000 3043 | 0.370 | 1.020 5483 | 0.000 4121 |
| .321 | .015 4637 ⁹⁶³ | 3063 ²⁰ | .371 | .020 6596 ¹¹¹³ | 4145 ²⁴ |
| .322 | .015 5602 ⁹⁶⁵ | 3083 ²⁰ | .372 | .020 7712 ¹¹¹⁶ | 4168 ²³ |
| .323 | .015 6571 ⁹⁶⁹ | 3103 ²⁰ | .373 | .020 8831 ¹¹¹⁹ | 4192 ²⁴ |
| .324 | .015 7542 ⁹⁷¹ | 3123 ²⁰ | .374 | .020 9953 ¹¹²² | 4216 ²⁴ |
| | | 975 ²⁰ | | | 1125 ²³ |
| 0.325 | 1.015 8517 | 0.000 3143 | 0.375 | 1.021 1078 | 0.000 4239 |
| .326 | .015 9494 ⁹⁷⁷ | 3163 ²⁰ | .376 | .021 2206 ¹¹²⁸ | 4263 ²⁴ |
| .327 | .016 0475 ⁹⁸¹ | 3183 ²⁰ | .377 | .021 3337 ¹¹³¹ | 4287 ²⁴ |
| .328 | .016 1458 ⁹⁸³ | 3204 ²¹ | .378 | .021 4471 ¹¹³⁴ | 4311 ²⁴ |
| .329 | .016 2445 ⁹⁸⁷ | 3224 ²⁰ | .379 | .021 5608 ¹¹³⁷ | 4335 ²⁴ |
| | | 989 ²⁰ | | | 1140 ²⁴ |
| 0.330 | 1.016 3434 | 0.000 3244 | 0.380 | 1.021 6748 | 0.000 4359 |
| .331 | .016 4427 ⁹⁹³ | 3265 ²⁰ | .381 | .021 7891 ¹¹⁴³ | 4383 ²⁴ |
| .332 | .016 5422 ⁹⁹⁵ | 3285 ²⁰ | .382 | .021 9037 ¹¹⁴⁶ | 4408 ²⁵ |
| .333 | .016 6421 ⁹⁹⁹ | 3306 ²¹ | .383 | .022 0186 ¹¹⁴⁹ | 4432 ²⁴ |
| .334 | .016 7422 ¹⁰⁰¹ | 3327 ²¹ | .384 | .022 1338 ¹¹⁵² | 4456 ²⁴ |
| | | 1005 ²¹ | | | 1155 ²⁵ |
| 0.335 | 1.016 8427 | 0.000 3348 | 0.385 | 1.022 2493 | 0.000 4481 |
| .336 | .016 9434 ¹⁰⁰⁷ | 3368 ²⁰ | .386 | .022 3651 ¹¹⁵⁸ | 4506 ²⁵ |
| .337 | .017 0445 ¹⁰¹¹ | 3389 ²¹ | .387 | .022 4812 ¹¹⁶¹ | 4530 ²⁴ |
| .338 | .017 1459 ¹⁰¹⁴ | 3410 ²² | .388 | .022 5977 ¹¹⁶⁵ | 4555 ²⁵ |
| .339 | .017 2475 ¹⁰¹⁶ | 3432 ²¹ | .389 | .022 7144 ¹¹⁶⁷ | 4580 ²⁵ |
| | | 1020 ²¹ | | | 1170 ²⁵ |
| 0.340 | 1.017 3495 | 0.000 3453 | 0.390 | 1.022 8314 | 0.000 4605 |
| .341 | .017 4517 ¹⁰²² | 3474 ²¹ | .391 | .022 9487 ¹¹⁷³ | 4630 ²⁵ |
| .342 | .017 5543 ¹⁰²⁶ | 3495 ²² | .392 | .023 0663 ¹¹⁷⁶ | 4655 ²⁵ |
| .343 | .017 6572 ¹⁰²⁹ | 3517 ²² | .393 | .023 1842 ¹¹⁷⁹ | 4680 ²⁵ |
| .344 | .017 7603 ¹⁰³¹ | 3538 ²¹ | .394 | .023 3025 ¹¹⁸³ | 4705 ²⁵ |
| | | 1035 ²² | | | 1185 ²⁵ |
| 0.345 | 1.017 8638 | 0.000 3560 | 0.395 | 1.023 4210 | 0.000 4730 |
| .346 | .017 9676 ¹⁰³⁸ | 3581 ²¹ | .396 | .023 5398 ¹¹⁸⁸ | 4756 ²⁶ |
| .347 | .018 0716 ¹⁰⁴⁰ | 3603 ²² | .397 | .023 6589 ¹¹⁹¹ | 4781 ²⁵ |
| .348 | .018 1760 ¹⁰⁴⁴ | 3624 ²¹ | .398 | .023 7784 ¹¹⁹⁵ | 4807 ²⁶ |
| .349 | .018 2807 ¹⁰⁴⁷ | 3646 ²² | .399 | .023 8981 ¹¹⁹⁷ | 4832 ²⁵ |
| | | 1049 ²² | | | 1200 ²⁶ |
| 0.350 | 1.018 3856 | 0.000 3668 | 0.400 | 1.024 0181 | 0.000 4858 |

TABLE 3.

| $\alpha^2 \sigma$ | J | K | $\alpha^2 \sigma$ | J | K |
|-------------------|----------------------------|--------------------------|-------------------|----------------------------|--------------------------|
| 0.400 | 1.024 0181 ¹²⁰⁴ | 0.000 4858 ²⁶ | 0.450 | 1.030 4040 ¹³⁵⁴ | 0.000 6244 ²⁹ |
| .401 | .024 1385 ¹²⁰⁶ | 4884 ²⁶ | .451 | .030 5394 ¹³⁵⁷ | 6273 ³⁰ |
| .402 | .024 2591 ¹²⁰⁹ | 4909 ²⁶ | .452 | .030 6751 ¹³⁶⁰ | 6303 ³⁰ |
| .403 | .024 3800 ¹²¹³ | 4935 ²⁶ | .453 | .030 8111 ¹³⁶³ | 6333 ³⁰ |
| .404 | .024 5013 ¹²¹⁵ | 4961 ²⁶ | .454 | .030 9474 ¹³⁶⁶ | 6363 ³⁰ |
| 0.405 | 1.024 6228 ¹²¹⁸ | 0.000 4987 ²⁷ | 0.455 | 1.031 0840 ¹³⁶⁹ | 0.000 6393 ³¹ |
| .406 | .024 7446 ¹²²² | 5014 ²⁶ | .456 | .031 2209 ¹³⁷² | 6424 ³⁰ |
| .407 | .024 8668 ¹²²⁴ | 5040 ²⁶ | .457 | .031 3581 ¹³⁷⁶ | 6454 ³⁰ |
| .408 | .024 9892 ¹²²⁸ | 5066 ²⁶ | .458 | .031 4957 ¹³⁷⁸ | 6484 ³¹ |
| .409 | .025 1120 ¹²³⁰ | 5092 ²⁷ | .459 | .031 6335 ¹³⁸¹ | 6515 ³⁰ |
| 0.410 | 1.025 2350 ¹²³³ | 0.000 5119 ²⁶ | 0.460 | 1.031 7716 ¹³⁸⁴ | 0.000 6545 ³¹ |
| .411 | .025 3583 ¹²³⁷ | 5145 ²⁷ | .461 | .031 9100 ¹³⁸⁸ | 6576 ³¹ |
| .412 | .025 4820 ¹²³⁹ | 5172 ²⁷ | .462 | .032 0488 ¹³⁹⁰ | 6607 ³¹ |
| .413 | .025 6059 ¹²⁴³ | 5199 ²⁶ | .463 | .032 1878 ¹³⁹³ | 6638 ³⁰ |
| .414 | .025 7302 ¹²⁴⁵ | 5225 ²⁷ | .464 | .032 3271 ¹³⁹⁷ | 6668 ³¹ |
| 0.415 | 1.025 8547 ¹²⁴⁹ | 0.000 5252 ²⁷ | 0.465 | 1.032 4668 ¹³⁹⁹ | 0.000 6699 ³² |
| .416 | .025 9796 ¹²⁵¹ | 5279 ²⁷ | .466 | .032 6067 ¹⁴⁰² | 6731 ³² |
| .417 | .026 1047 ¹²⁵⁵ | 5306 ²⁷ | .467 | .032 7469 ¹⁴⁰⁶ | 6762 ³¹ |
| .418 | .026 2302 ¹²⁵⁸ | 5333 ²⁸ | .468 | .032 8875 ¹⁴⁰⁸ | 6793 ³¹ |
| .419 | .026 3560 ¹²⁶⁰ | 5361 ²⁷ | .469 | .033 0283 ¹⁴¹¹ | 6824 ³² |
| 0.420 | 1.026 4820 ¹²⁶⁴ | 0.000 5388 ²⁸ | 0.470 | 1.033 1694 ¹⁴¹⁵ | 0.000 6856 ³¹ |
| .421 | .026 6084 ¹²⁶⁶ | 5415 ²⁷ | .471 | .033 3109 ¹⁴¹⁷ | 6887 ³¹ |
| .422 | .026 7350 ¹²⁷⁰ | 5443 ²⁷ | .472 | .033 4526 ¹⁴²¹ | 6919 ³² |
| .423 | .026 8620 ¹²⁷³ | 5470 ²⁸ | .473 | .033 5947 ¹⁴²³ | 6950 ³¹ |
| .424 | .026 9893 ¹²⁷⁵ | 5498 ²⁷ | .474 | .033 7370 ¹⁴²⁷ | 6982 ³² |
| 0.425 | 1.027 1168 ¹²⁷⁹ | 0.000 5525 ²⁸ | 0.475 | 1.033 8797 ¹⁴²⁹ | 0.000 7014 ³² |
| .426 | .027 2447 ¹²⁸² | 5553 ²⁸ | .476 | .034 0226 ¹⁴³³ | 7046 ³² |
| .427 | .027 3729 ¹²⁸⁴ | 5581 ²⁸ | .477 | .034 1659 ¹⁴³⁵ | 7078 ³² |
| .428 | .027 5013 ¹²⁸⁸ | 5609 ²⁸ | .478 | .034 3094 ¹⁴³⁹ | 7110 ³² |
| .429 | .027 6301 ¹²⁹¹ | 5637 ²⁸ | .479 | .034 4533 ¹⁴⁴¹ | 7142 ³³ |
| 0.430 | 1.027 7592 ¹²⁹³ | 0.000 5665 ²⁸ | 0.480 | 1.034 5974 ¹⁴⁴⁵ | 0.000 7175 ³² |
| .431 | .027 8885 ¹²⁹⁷ | 5693 ²⁸ | .481 | .034 7419 ¹⁴⁴⁸ | 7207 ³³ |
| .432 | .028 0182 ¹³⁰⁰ | 5721 ²⁹ | .482 | .034 8867 ¹⁴⁵⁰ | 7240 ³³ |
| .433 | .028 1482 ¹³⁰³ | 5750 ²⁹ | .483 | .035 0317 ¹⁴⁵⁴ | 7272 ³² |
| .434 | .028 2785 ¹³⁰⁶ | 5778 ²⁸ | .484 | .035 1771 ¹⁴⁵⁷ | 7305 ³² |
| 0.435 | 1.028 4091 ¹³⁰⁸ | 0.000 5806 ²⁹ | 0.485 | 1.035 3228 ¹⁴⁵⁹ | 0.000 7337 ³³ |
| .436 | .028 5399 ¹³¹² | 5835 ²⁹ | .486 | .035 4687 ¹⁴⁶³ | 7370 ³³ |
| .437 | .028 6711 ¹³¹⁵ | 5864 ²⁸ | .487 | .035 6150 ¹⁴⁶⁶ | 7403 ³³ |
| .438 | .028 8026 ¹³¹⁸ | 5892 ²⁹ | .488 | .035 7616 ¹⁴⁶⁹ | 7436 ³³ |
| .439 | .028 9344 ¹³²¹ | 5921 ²⁹ | .489 | .035 9085 ¹⁴⁷¹ | 7469 ³³ |
| 0.440 | 1.029 0665 ¹³²⁴ | 0.000 5950 ²⁹ | 0.490 | 1.036 0556 ¹⁴⁷⁵ | 0.000 7502 ³⁴ |
| .441 | .029 1989 ¹³²⁷ | 5979 ²⁹ | .491 | .036 2031 ¹⁴⁷⁸ | 7536 ³³ |
| .442 | .029 3316 ¹³³⁰ | 6008 ²⁹ | .492 | .036 3509 ¹⁴⁸¹ | 7569 ³³ |
| .443 | .029 4646 ¹³³³ | 6037 ²⁹ | .493 | .036 4990 ¹⁴⁸⁴ | 7602 ³³ |
| .444 | .029 5979 ¹³³⁶ | 6066 ³⁰ | .494 | .036 6474 ¹⁴⁸⁷ | 7636 ³⁴ |
| 0.445 | 1.029 7315 ¹³³⁹ | 0.000 6096 ²⁹ | 0.495 | 1.036 7961 ¹⁴⁸⁹ | 0.000 7670 ³³ |
| .446 | .029 8654 ¹³⁴² | 6125 ²⁹ | .496 | .036 9450 ¹⁴⁹³ | 7703 ³⁴ |
| .447 | .029 9996 ¹³⁴⁵ | 6155 ³⁰ | .497 | .037 0943 ¹⁴⁹⁶ | 7737 ³⁴ |
| .448 | .030 1341 ¹³⁴⁸ | 6184 ³⁰ | .498 | .037 2439 ¹⁴⁹⁹ | 7771 ³⁴ |
| .449 | .030 2689 ¹³⁵¹ | 6214 ³⁰ | .499 | .037 3938 ¹⁵⁰² | 7805 ³⁴ |
| 0.450 | 1.030 4040 | 0.000 6244 | 0.500 | 1.037 5440 | 0.000 7839 |

TABLE 3.

| $\alpha^{\dagger}\sigma$ | J | K | $\alpha^{\dagger}\sigma$ | J | K |
|--------------------------|---------------------------|--------------------|--------------------------|---------------------------|--------------------------|
| 0.500 | 1.037 5440 | 0.000 7839 | 0.550 | 1.045 4393 | 0.000 9659 |
| .501 | .037 6945 ¹⁵⁰⁵ | 7873 ³⁴ | .551 | .045 6049 ¹⁶⁵⁶ | 9698 ³⁹ |
| .502 | .037 8453 ¹⁵⁰⁸ | 7907 ³⁴ | .552 | .045 7708 ¹⁶⁵⁹ | 9737 ³⁹ |
| .503 | .037 9964 ¹⁵¹¹ | 7942 ³⁵ | .553 | .045 9370 ¹⁶⁶² | 9776 ³⁹ |
| .504 | .038 1478 ¹⁵¹⁴ | 7976 ³⁴ | .554 | .046 1036 ¹⁶⁶⁶ | 9815 ³⁹ |
| | 1518 | 35 | | 1668 | |
| 0.505 | 1.038 2996 | 0.000 8011 | 0.555 | 1.046 2704 | 0.000 9854 |
| .506 | .038 4516 ¹⁵²⁰ | 8045 ³⁴ | .556 | .046 4375 ¹⁶⁷¹ | 9894 ⁴⁰ |
| .507 | .038 6039 ¹⁵²³ | 8080 ³⁵ | .557 | .046 6049 ¹⁶⁷⁴ | 9933 ³⁹ |
| .508 | .038 7565 ¹⁵²⁶ | 8115 ³⁵ | .558 | .046 7727 ¹⁶⁷⁸ | 0.000 9972 ³⁹ |
| .509 | .038 9094 ¹⁵²⁹ | 8150 ³⁵ | .559 | .046 9407 ¹⁶⁸⁰ | 0.001 0012 ⁴⁰ |
| | 1532 | 35 | | 1683 | 40 |
| 0.510 | 1.039 0626 | 0.000 8185 | 0.560 | 1.047 1090 | 0.001 0052 |
| .511 | .039 2162 ¹⁵³⁶ | 8220 ³⁵ | .561 | .047 2777 ¹⁶⁸⁷ | 0092 ⁴⁰ |
| .512 | .039 3700 ¹⁵³⁸ | 8255 ³⁵ | .562 | .047 4466 ¹⁶⁸⁹ | 0131 ³⁹ |
| .513 | .039 5241 ¹⁵⁴¹ | 8290 ³⁵ | .563 | .047 6159 ¹⁶⁹³ | 0171 ⁴⁰ |
| .514 | .039 6785 ¹⁵⁴⁴ | 8325 ³⁵ | .564 | .047 7854 ¹⁶⁹⁵ | 0211 ⁴⁰ |
| | 1548 | 36 | | 1699 | 41 |
| 0.515 | 1.039 8333 | 0.000 8361 | 0.565 | 1.047 9553 | 0.001 0252 |
| .516 | .039 9883 ¹⁵⁵⁰ | 8396 ³⁵ | .566 | .048 1254 ¹⁷⁰¹ | 0292 ⁴⁰ |
| .517 | .040 1436 ¹⁵⁵³ | 8432 ³⁶ | .567 | .048 2959 ¹⁷⁰⁵ | 0332 ⁴⁰ |
| .518 | .040 2993 ¹⁵⁵⁷ | 8468 ³⁶ | .568 | .048 4666 ¹⁷⁰⁷ | 0373 ⁴¹ |
| .519 | .040 4552 ¹⁵⁵⁹ | 8503 ³⁵ | .569 | .048 6377 ¹⁷¹¹ | 0413 ⁴⁰ |
| | 1563 | 36 | | 1714 | 41 |
| 0.520 | 1.040 6115 | 0.000 8539 | 0.570 | 1.048 8091 | 0.001 0454 |
| .521 | .040 7680 ¹⁵⁶⁵ | 8575 ³⁶ | .571 | .048 9807 ¹⁷¹⁶ | 0495 ⁴¹ |
| .522 | .040 9248 ¹⁵⁶⁸ | 8611 ³⁶ | .572 | .049 1527 ¹⁷²⁰ | 0536 ⁴¹ |
| .523 | .041 0820 ¹⁵⁷² | 8647 ³⁶ | .573 | .049 3250 ¹⁷²³ | 0577 ⁴¹ |
| .524 | .041 2394 ¹⁵⁷⁴ | 8684 ³⁷ | .574 | .049 4975 ¹⁷²⁵ | 0618 ⁴¹ |
| | 1578 | 36 | | 1729 | 41 |
| 0.525 | 1.041 3972 | 0.000 8720 | 0.575 | 1.049 6704 | 0.001 0659 |
| .526 | .041 5553 ¹⁵⁸¹ | 8756 ³⁶ | .576 | .049 8436 ¹⁷³² | 0700 ⁴¹ |
| .527 | .041 7136 ¹⁵⁸³ | 8793 ³⁷ | .577 | .050 0171 ¹⁷³⁵ | 0741 ⁴¹ |
| .528 | .041 8723 ¹⁵⁸⁷ | 8830 ³⁷ | .578 | .050 1909 ¹⁷³⁸ | 0783 ⁴² |
| .529 | .042 0312 ¹⁵⁸⁹ | 8866 ³⁶ | .579 | .050 3650 ¹⁷⁴¹ | 0824 ⁴¹ |
| | 1593 | 37 | | 1744 | 42 |
| 0.530 | 1.042 1905 | 0.000 8903 | 0.580 | 1.050 5394 | 0.001 0866 |
| .531 | .042 3501 ¹⁵⁹⁶ | 8940 ³⁷ | .581 | .050 7140 ¹⁷⁴⁶ | 0908 ⁴² |
| .532 | .042 5099 ¹⁵⁹⁸ | 8977 ³⁷ | .582 | .050 8890 ¹⁷⁵⁰ | 0950 ⁴² |
| .533 | .042 6701 ¹⁶⁰² | 9014 ³⁷ | .583 | .051 0643 ¹⁷⁵³ | 0992 ⁴² |
| .534 | .042 8306 ¹⁶⁰⁵ | 9051 ³⁷ | .584 | .051 2399 ¹⁷⁵⁶ | 1034 ⁴² |
| | 1608 | 38 | | 1759 | 42 |
| 0.535 | 1.042 9914 | 0.000 9089 | 0.585 | 1.051 4158 | 0.001 1076 |
| .536 | .043 1524 ¹⁶¹⁰ | 9126 ³⁷ | .586 | .051 5921 ¹⁷⁶³ | 1118 ⁴² |
| .537 | .043 3138 ¹⁶¹⁴ | 9164 ³⁸ | .587 | .051 7686 ¹⁷⁶⁵ | 1161 ⁴³ |
| .538 | .043 4755 ¹⁶¹⁷ | 9201 ³⁷ | .588 | .051 9454 ¹⁷⁶⁸ | 1203 ⁴² |
| .539 | .043 6375 ¹⁶²⁰ | 9239 ³⁸ | .589 | .052 1225 ¹⁷⁷¹ | 1246 ⁴³ |
| | 1623 | 37 | | 1774 | 42 |
| 0.540 | 1.043 7998 | 0.000 9276 | 0.590 | 1.052 2999 | 0.001 1288 |
| .541 | .043 9624 ¹⁶²⁶ | 9314 ³⁸ | .591 | .052 4776 ¹⁷⁷⁷ | 1331 ⁴³ |
| .542 | .044 1253 ¹⁶²⁹ | 9352 ³⁸ | .592 | .052 6557 ¹⁷⁸¹ | 1374 ⁴³ |
| .543 | .044 2884 ¹⁶³¹ | 9390 ³⁸ | .593 | .052 8340 ¹⁷⁸³ | 1417 ⁴³ |
| .544 | .044 4519 ¹⁶³⁵ | 9428 ³⁸ | .594 | .053 0128 ¹⁷⁸⁶ | 1460 ⁴³ |
| | 1638 | 39 | | 1790 | 43 |
| 0.545 | 1.044 6157 | 0.000 9467 | 0.595 | 1.053 1916 | 0.001 1503 |
| .546 | .044 7798 ¹⁶⁴¹ | 9505 ³⁸ | .596 | .053 3708 ¹⁷⁹² | 1547 ⁴⁴ |
| .547 | .044 9443 ¹⁶⁴⁵ | 9543 ³⁸ | .597 | .053 5503 ¹⁷⁹⁵ | 1590 ⁴³ |
| .548 | .045 1090 ¹⁶⁴⁷ | 9582 ³⁹ | .598 | .053 7302 ¹⁷⁹⁹ | 1633 ⁴³ |
| .549 | .045 2740 ¹⁶⁵⁰ | 9621 ³⁹ | .599 | .053 9103 ¹⁸⁰¹ | 1677 ⁴⁴ |
| | 1653 | 38 | | 1805 | 44 |
| 0.550 | 1.045 4393 | 0.000 9659 | 0.600 | 1.054 0908 | 0.001 1721 |

AN OCCURRENCE OF BOUDINAGE STRUCTURE IN NEW SOUTH WALES.

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With three text-figures.

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INTRODUCTION.

During an investigation of the geology of the Wantabadgery district, New South Wales, certain masses of quartzitic material roughly elliptical in section were observed interbedded with more argillaceous low-grade metamorphic rocks in the vicinity of Mundarlo (for locality see Fig. 1, inset). The arrangement resembles the structure called *boudinage* by Lohest (1909). Boudinage structures have not often been reported by geologists, in Australia at any rate, and it was therefore thought desirable to place the present occurrence on record. The aim of this note is to record the new locality and to give a brief description of the structure. Oriented specimens have been collected for the purpose of a petrofabric examination, but this has not yet been commenced.

GENERAL GEOLOGICAL RELATIONS.

The country rocks for the most part consist of rather thick interbedded sandy and argillaceous beds believed to be of Upper Ordovician age, though reliable palaeontological evidence is lacking within the area examined. Sedimentary types, corresponding to the pelites, psammopelites and psammites, recognised by Joplin at Cooma (Joplin, 1942) and Albury, are present, but the psammopelites are quite the most abundant. These sediments are now represented by phyllites, mica-schists, quartzites and quartz-rich granulites of epimetamorphic type. The *terrain* has been invaded by a mass of partly gneissic biotite-granite, lithologically similar to the Cooma gneiss (Joplin, 1942), which is considered to be of epi-Ordovician age. Within the contact areole of this granite the argillaceous schists have developed conspicuous knots of porphyroblastic andalusite and cordierite.

At the present time the structure of the area is far from being clear. Field-relations suggest that the bedded rocks have been tightly, almost isoclinally, folded on axes generally parallel to the north-west-south-east strike of the country. Dips are constantly steep, often nearly vertical, and the cleavage developed in the argillaceous phyllites and schists is usually parallel to the bedding.

THE BOUDINAGE STRUCTURES.

The boudins have been found in a restricted area along the dry creek in Pors. 97, 98, 169, Parish of Mundarlo, Co. Wynyard. Most of them occur in the banks of the creek, where it locally cuts across the strike of the country. All the observed outcrops are within the zone of knotted schists (Fig. 1). The structures appear only where there is a rapid alternation of psammitic and more argillaceous beds and in the vicinity of the best-developed boudins the average thickness of individual horizons is only about 2-3 inches. A few boudin-like

blocks up to 8 inches thick have been observed in the same locality, but the field-relations are not clear. This close bedding is in contrast with the greater part of the sedimentary series in this region, where much thicker beds are the

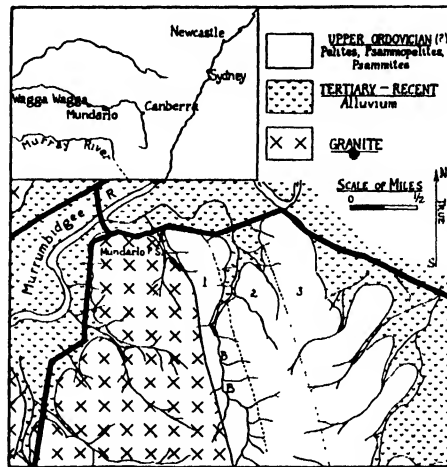


Fig. 1.—Geological sketch-map of the Mundarlo District. Metamorphic zones shown thus: Zone of Knotted Schists (1); Biotite Zone (2); Chlorite-sericite Zone (3). Boudinage occurrences indicated by (B).

general rule. The material of which the boudins are composed is typically a rather compact, fine-grained, slightly mottled cream to grey psammite. In thin section it is seen to consist essentially of quartz and clinozoisite-epidote with a

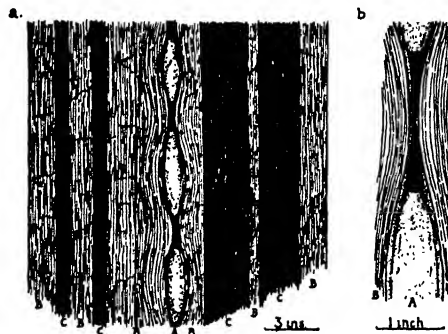


Fig. 2.

- (a) Typical arrangement of boudinage at Mundarlo. From a photograph.
 (b) The neck between two small boudins showing parallel cracks. Psammite (A), Psammopelite (B), Knotted Schist (pelite) (C). The black marks at the nodes of the boudins represent quartz veins.

general granulitic appearance. The original sediment was probably a calcareous or marly sandstone, a relatively rare type in this region. It is interesting to note that ellipsoids of epidosite have been recorded at Broken Hill (Browne, 1922). Their origin and significance are, however, not clear.

The Mundarlo boudins are strung out along the bedding and are only found between more argillaceous bands. Figure 2a illustrates the best-exposed section. The major axes are parallel to the bedding and are usually about twice or three times as great as the minor axes, the average dimensions being about 4 inches and 1.5 to 2 inches respectively. Each boudin is joined laterally to its fellow by a narrow neck composed of the same material as the main body. Fractures have developed within the necks, and towards the shoulders some of these cracks are parallel to the margins of the boudins. An extreme case of this parallel cracking is to be seen in Fig. 2b. These nodal fractures are always filled with glassy quartz which usually does not enter the neighbouring beds. These adjacent beds have a definite cleavage curved parallel to the margins of the boudins. The effect is most marked at the nodal positions. The undulations along the bedding caused by the alternate thickening and thinning of the psammite band are evened out in the immediately contiguous horizons (above and below). Rarely does the disturbance proceed appreciably beyond these two beds.

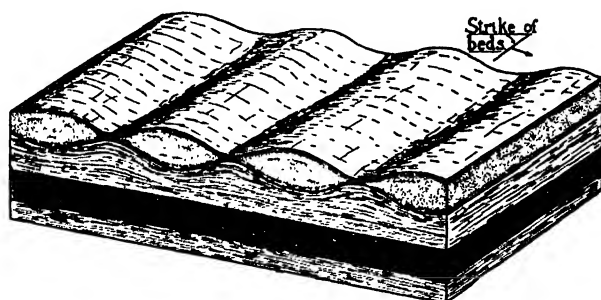


Fig. 3.—Diagrammatic representation of the probable nature of the Mundarlo boudinage.

The third-dimensional aspect of these structures is not altogether satisfactory because the bedding-planes are not uncovered where the boudins outcrop. However, several specimens of boudins have been removed with a geological pick and they appear to be end-sections of elongated masses somewhat similar to the barrels or "sausages" of the classic boudinage of Lohest, but they are very much more flattened than the type-specimens. Figure 3 gives a diagrammatic view of the probable nature of the boudins. They seem to trend almost horizontally along the bedding-planes, and are thus nearly normal to the dip direction of the beds. The length of the boudins is unknown. A faint striation roughly normal to the length of the boudins is a constant feature but there is not much indication of lineation parallel to the flattened barrels. Similar lineation down the dip has been observed on the s-surfaces of specimens from the same area, which, however, show no signs of boudinage.

DISCUSSION.

The term *boudinage* was first applied to regular, nearly cylindrical bodies of sandstone lying in the bedding-planes of the Devonian strata in the Bastogne district, Belgium. These cylinders or boudins are separated from each other by sharp fractures, transverse to the bedding, and filled by spindle-shaped quartz-veins. The adjacent less competent beds have flowed into the depressions between the boudins, which appear as regular undulations on the bedding surfaces. In more intensely metamorphosed *terrains*, such as Scandinavia, boudinage structures have been recorded, but often they present certain modifications of the classical examples. The columns are commonly flattened with the

major axis of cross-section parallel to the bedding. The quartz septa between boudins are more typically irregular in shape. Wegmann (1932) gives some illustrations of such modified structures. As an extreme stage Corin (1932) refers to the "*quartzites en amandes*" from the Ardennes, which were figured by Gosselet (1888, Pl. V, No. 5). The structures described in the present note rather resemble Gosselet's examples, although they are not as extreme as the "*amandes*".

Several different explanations have been advanced to account for the origin of boudinage. These have been outlined briefly by Read (1934), who, agreeing with Corin and Wegmann, concludes that the arrangement was caused by extension in alternating competent and incompetent beds. Cloos (1946) tacitly accepts this interpretation. In his example of boudinage from Unst Read (1934) proved that the extension of the beds was due to a compressive force acting normal to the direction of stretching. Corin (1932), in his work, attributed the effect to an oblique force, the component of which on the bedding-plane was parallel to the direction of extension. In both cases, however, the result of the extension is that the competent bands are broken by transverse fractures whilst the less competent adjacent beds flow towards the gaps caused by the bending in of the edges of the resistant blocks. Quartz is simultaneously deposited in the fractures.

In the boudinage from Mundarlo a relatively great extension is indicated. The original psammitic bands were fractured but the marginal parts of the same beds were induced to flow past the ends of the broken blocks, which at the same time moved apart. The attenuated necks thus produced are in sharp contrast with the clear-cut fractures of the Belgian boudinage. It is possible that the marked secondary flow bears some causal relation to the composition of the "boudined" beds. True quartzites are not common in the vicinity of the boudinage and so no comparative estimate can be made of the influence of the lime-bearing minerals in the boudins. The cause of the extension is not yet certain. The most plausible suggestion is that the boudins occur on the limb (or limbs) of a tight fold in which there was extension normal to the axis. If, as seems likely, the folding was related to the metamorphism of the area, the flowage of the beds may have been greatly aided by the increased pressure-temperature conditions. However, many more data are required before any reliable statement can be made.

SUMMARY.

An occurrence of boudinage structure in the Upper Ordovician of the Mundarlo district, New South Wales, is recorded. The examples are small but nevertheless indicate appreciable flowage. As far as it can be seen the boudins lie parallel to the strike of the enclosing beds. The cause of the extension which produced the structures is not certain.

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ENERGY TRANSACTIONS IN HOMEOTHERMIC ANIMALS.*

By HEDLEY R. MARSTON, F.R.S.

Mr. President and Members of the Royal Society of New South Wales,

I thank you for the honour of being selected by you to be the Liversidge Research Lecturer for 1950. I had never an opportunity to meet Archibald Liversidge, but I knew of his devotion to Science, and so was gratified when this opportunity made it possible for me to help carry out the desires expressed in his last testament. In this you will recall, Liversidge, with deep insight, set down the reference that "... the lectures shall be such as will *encourage research* and *stimulate the lecturer* and the public to think and acquire new knowledge by research, instead of merely giving instruction in what is already known . . . " Your lecturer has been stimulated in the course of the preparation of this discourse for you : if what it contains entices any one of you to use his special skill to render more clear the chemical reactions that are responsible for energy transfer in living organisms, the hopes of Liversidge will be met.

An exhaustive discussion of the field of knowledge that it would be desirable to cover before we might be quite ready to consider what is now known of the chemical reactions involved in the energy transactions of living processes is not for this occasion, so I trust I shall be forgiven if the treatment of the subject lacks the nicety of balance which may have been achieved had the facts we have at our disposal justified more precise generalization.† But we shall, no doubt, occasionally catch a glimpse, however faint, of the general laws of energy exchange that operate in living material, and thus be encouraged to add to the pattern of knowledge that is already taking shape.

In the somewhat dismal prospect revealed by Clausius' conclusion that our world is ever moving towards a state of maximum entropy, there is one bright spot. Photosynthesis, by those autotrophic organisms which bear chlorophyll, converts a part of solar radiation into chemical energy of high potential and so initiates a series of reactions which create order out of the monotony of the more probable state that atoms of hydrogen, oxygen, carbon, nitrogen, etc., have long since assumed in the earth's atmosphere and hydrosphere. The continual renewal of life brought about in this way is a backwater contrary to the flow towards the equilibrium implied in maximum entropy ; but this state is transient—chemical reactions of living processes are poised precariously in a medium of oxygen which, although for a while their main driving force, ultimately consumes the organism that renders them possible, to degrade its ordered substance again to Nature's more probable state. Transient and somewhat feeble this contra current, but it flows to a complexity of form in which stirs thought, the mirror in which Nature views herself. We are tempted to dwell here and ask questions. Uncertain ground this, however, and perilously near the siren call of first causes. So on this occasion let us avoid it and devote our

* The Liversidge Research Lecture delivered November 15th, 1950.

† I hope to be forgiven also for failing to mention the names of those responsible for the great volume of experimental work drawn on during the preparation of this lecture. To acknowledge even briefly those whose contributions have given form to this subject would call for a catalogue of names that would increase many times the length of this paper.

attention to phenomena—nowise less alluring to the curious—which may be interpreted through experimental enquiry.

I propose to recall for you some of the phenomena associated with the overall energy transactions that take place under conditions of relatively constant temperature in the tissues of homeothermic animals; to seek with you to learn something of the efficiency with which these proceed; and then to view our findings in the light of what is now known of the chemical reactions of intermediary metabolism that give rise to the free energy utilized in the process of living.

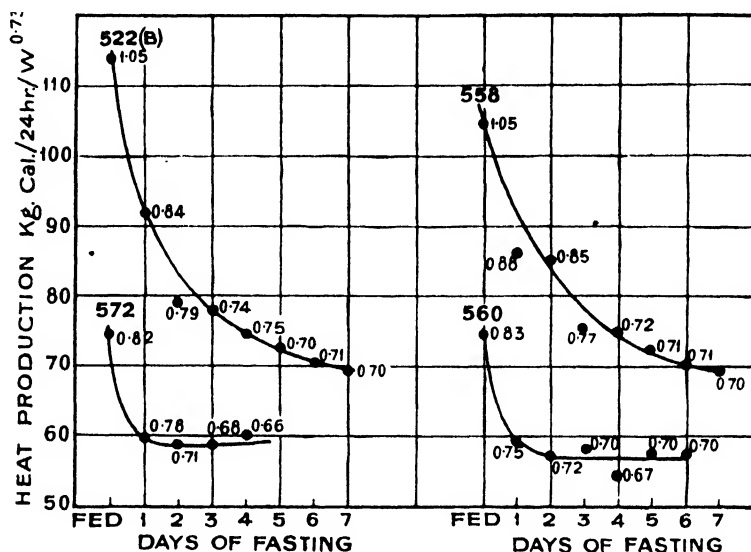


Fig. 1.—The fall in the rate of heat production that supervenes on fasting is shown by the performance of four sheep, of which two, Nos. 522B and 558, were fasted after three months on a very high level of feeding, and two, Nos. 572 and 560, after a similar period on rations which provided sufficient energy to meet only 50 per cent. of their energy requirements.

The gradual fall in the rate of energy expenditure of Nos. 522B and 558 towards the asymptote of the basal level is typical of well fed ruminants; the slow recession being due to the buffer effect of the voluminous rumen contents, which continues to ferment and so to provide assimilable nutriment to the animal for several days after the beginning of fasting. As carnivores and mixed-feeders rapidly digest and assimilate their food, the enhanced rate of heat production brought about by the heat increment of the absorbed nutriment subsides within 12–18 hours after feeding, and so the recession to the basal level is precipitate. Subsequent to reaching the basal level, the rate of heat production of the resting animal remains unaltered for a considerable period.

Sheep Nos. 572 and 560 were already in a state of malnutrition when the observations were commenced. As they were fasted from a low level of food intake, the residual food in the rumen was small, and fermentation was complete in 48 hours, and so the rate of heat production in these fell more rapidly to the low “basal” level, which is a consequence of inanition.

The respiratory quotient of each animal during the 24 hours over which its heat output was estimated is reported at each point on the graphs.

It is not my intention to pause long in the dawn of the modern era of nutritional physiology, but our thesis will be better founded if we recall Antoine Lavoisier's last great contribution to science—his discovery of a relationship between the work performed by an animal and the oxygen it consumes—for this was indeed the sunrise. Perusal of the memoir in which Lavoisier describes the experiments that led to these conclusions still quickens the pulse, for he so

clearly delights in setting down his ideas. Here, in a manner quite foreign to his earlier writings, he exults in his argument, then, to savour it, pauses a while to philosophize, akin in style to that incorrigible moralizer Joseph Priestly; soon to take up the threads again to discuss the effects of the ingestion of food on oxygen consumption—which incidentally will be our main concern—finally to end with an excursion into politics, pleading men to caution in the threatening storm of revolution, as if in anticipation of his own fate. This, the last and greatest of his memoirs to the Academy, contains his confession of faith; in it he sets down two essential conditions for the advancement of knowledge—freedom of thought and the quietness of the laboratory. In the light of his experiments he had beheld the vista and declared: “*La vie est une fonction chimique*”.

Before we consider the classical theories of energy metabolism, and attempt to set them more securely in the framework of existing biochemical knowledge, we should recall the main phenomena associated with heat production in homeothermic animals. At this stage our concern is neither with the energy expended in voluntary muscular movement nor with the processes that are influenced through nervous and hormonal mechanisms when, in a cold environment, radiation exceeds the amount of heat liberated in the normal course of the animal's metabolism. We seek at this juncture to learn something of the rate of energy expenditure necessary merely to sustain life in the homeothermic animal, and so are at pains to eliminate as many variables as possible.

When the increased heat production that supervenes on consumption of food has subsided, a warm-blooded animal, at rest in a neutral thermal environment, produces heat at a rate which for some days is tolerably uniform. During prolonged fasting—while the organism is virtually living at the expense of its own tissues—this basal rate of heat production recedes very gradually with the onset of inanition, to increase abruptly, as a symptom of the cataclysmic disorganization of the metabolic processes, immediately prior to death.

Some of the earliest observations, made over 100 years ago, showed clearly that this overall cost of living is not a direct mathematical function of the animal's size but is nearly proportional to its body surface. Literal acceptance of the Surface Law which was formulated from this observed relationship has been responsible for no little confusion. The search for a parameter to facilitate comparison of the metabolic behaviour of animals of different sizes was influenced by the implication that radiation from the body surface determines the basal rate of heat production. In consequence, elaborate measurements were made of the areas of body surfaces in order to relate them to body weights so that—questionable logic this—energy metabolism might be related to surface areas computed from body weights. All this in search of a chimera, for any generalization based on the assumption that equal areas result in equal heat losses is precluded by the widely different capacities of different parts of the body surface to radiate heat. The Surface Law, in so far as it suggests a causal relationship between the physical surface of an animal and its basal rate of heat production, is untenable.

There is, however, no question that basal metabolism varies exponentially with body weight. In homeothermic animals a relationship of this sort is clearly essential. A few simple calculations of heat exchange will suffice to indicate the necessity for the relatively great differences between the rates at which heat is produced in small and large animals. A mouse, for instance, with a basal rate of heat production per unit weight identical with that of an elephant could not live as a warm blooded animal in a temperate climate unless—strange fancy this—it were clothed in an envelope some 30 cm. thick of material with the same specific insulation as fur; or conversely, an elephant with a metabolic

rate per unit weight identical with that of a mouse could not exist in its native habitat without a radiator of monstrous proportions. These are extremes in the phylogenetic scale, but within small limits of deviation the same exponential relationship holds for all homeothermic animals, of identical species and of different species, whatever their size.

Some such relationship could not have been other than a prime criterion which, in the course of Evolution, determined survival of the species. The precision with which Natural Selection has poised the rate of metabolism and has graded so nicely the subsidiary anatomical apparatus to fulfil its requirements of fuel and oxygen is a subject for wonder. All seems so perfectly ordered, as if one agency determines both the size and the metabolic rate of the animal;

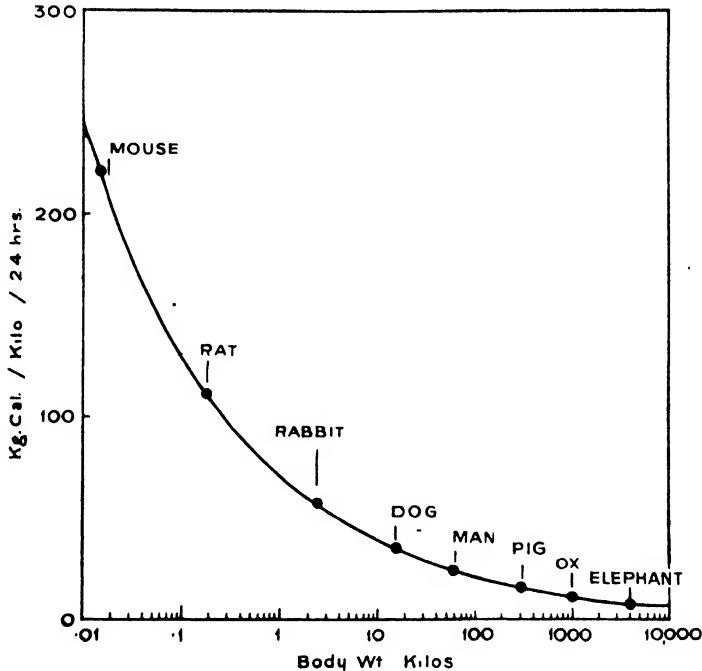


Fig. 2.—The relationship between body weight and the rate of heat production of homeothermic animals under basal conditions is plotted. The points are mean values of critical determinations. The logarithmic scale employed for the ordinate of body weights tends to obscure small deviations from the smooth curve, but there is no doubt of the overall exponential relationship.

for in such close harmony we are led to seek a single variable. Our thoughts at once fly to hormonal balance within the organism, and particularly to thyroxine with its known profound effects on both heat production and metabolism of protein, and incidentally on growth and development. But to follow such thoughts at this stage would lead us to digress. We shall return to them later.

We may accept, then, that the energy costs involved in living under basal conditions vary exponentially with the weight of the animal. Observation of the metabolism of animals varying in size from that of a mouse to that of the elephant suggest that the rate of heat production by mature animals under basal conditions will not deviate far from $70 W^{0.7}$ Kg. Cal. per 24 hours, where W (Kg.) is the body weight of the fasting animal. As this is an empiric expression determined from well observed experimental data, it implies no causal relationships. It is subject to small intraspecific corrections for age, sex, etc., which factors are known to influence metabolic activities.

In these considerations of the overall heat production we are dealing with a summation of the rates at which heat is produced by a number of different organs which, having in the course of ontogenesis assumed distinct functions, might be expected, *a priori*, to differ in their call for energy. Let us then examine the contributions made by individual organs to the overall heat production. A close estimate may be made of this from the rates of oxygen consumption and carbon dioxide formation, and these may be assessed directly from the rate of blood flow and the difference in composition of the arterial and venous supply to individual organs. The rate of heat production in the visceral organs is amazingly great. Under basal conditions, approximately 70 per cent. of the total heat production of man, for example, originates in the heart, kidneys, liver and brain, the combined weights of which constitute little over 5 per cent. of the total body weight (*vide* Table 1). The relatively rapid rate of heat production

TABLE I.
Energy Dissipated by the Tissues of a 70 Kg. Man under "Basal" Conditions.

| Tissue. | Weight of Organ and (Proportion of Body Weight). | Oxygen Consumption of Organ Litres O ₂ /24 hr. and (Proportion of Total Oxygen Consumption). | Heat Produced. Kg. Cal./24 hr./Kg. Tissue. |
|-------------------------|--|--|--|
| Whole body | 70 Kg. (100 per cent.) | 356 (100 per cent.) | 23·5 |
| Heart .. . | 0·33 Kg. (0·47 per cent.) | 37 (10 per cent.) | 520 |
| Kidneys .. . | 0·33 Kg. (0·47 per cent.) | 31 (9 per cent.) | 440 |
| Liver .. . | 1·6 Kg. (2·3 per cent.) | 115 (32 per cent.) | 335 |
| Brain .. . | 1·4 Kg. (2 per cent.) | 68·5 (19 per cent.) | 225 |
| | 3·66 Kg. (5·24 per cent.) | 251·5 (70 per cent.) | |
| Rest of body (by diff.) | 66·3 Kg. (94·7 per cent.) | 105 (30 per cent.) | 7·4 |
| Muscles .. . | 29·5 Kg. (42 per cent.) | 58·5 (16 per cent.) | 9·2 |

by the heart is not surprising—the work entailed in circulating the blood of a man of 70 Kg. body weight, for example, accounts for approximately 45 Kg. Cal./24 hr., which from the overall heat production implies a mechanical efficiency of close to 25 per cent. And the kidneys have extraneous work to do. Here again there is nothing to astonish us until we compute the free energy change entailed in the transport of salts, urea and water between the blood plasma and the urine, and find that the osmotic work necessary for the secretion of urine amounts to little more than 1 per cent. of the energy liberated as heat by the kidneys. Thus in the kidneys as well as in the liver and, curiously, in the brain, relatively intense chemical work proceeds continually, even when the animal is fasting and at rest. The chemical activity within these organs under basal conditions accounts for about 60 per cent. of the total heat produced by the animal. In comparison, the energy necessary to sustain the skeletal muscles in a living condition is small, smaller in fact than is implied in Table 1, because,

even when at rest, postural tonus involves some work. Why then this comparatively great intensity of activity in the visceral organs? What are the reactions which expend fuel at such a rate? And what controls them so precisely?

Before we seek an answer to these questions we might with profit consider briefly the phenomena associated with the increased heat production that supervenes on feeding. Up to this stage our concern has been with the *rate* of heat production under conditions selected in attempt to ensure a minimum expenditure of energy. This basal rate, however, is not by any means a simple expression of the minimum rate of free energy expenditure necessary to sustain

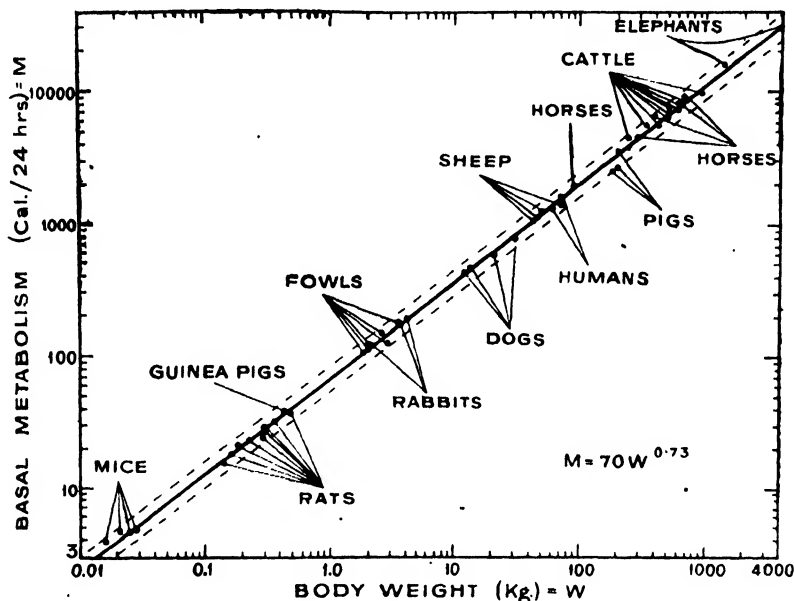


Fig. 3.—The exponential relationship between the body weight and the rated heat production of homeothermic animals under basal conditions is obvious from the above figure. The heavy line is that of the expression $M = 70W^{0.73}$ in which M is the rate of heat production in Kg. Cal./24 hr. and W is the body weight in Kg. The expression, derived empirically from observed data, is the best fit over a wide range of animals, the body weights of which extend from 20 gm. to 4×10^6 gm. The significance of the second figure of the exponent is doubtful. The broken lines are to indicate 10 per cent. deviation from the expression.

life in the organism. Such an assumption would imply that the combustible energy of the materials drawn from the tissues of the fasting animal to support the living processes is 100 per cent. efficient for this purpose. Clearly, when considering energy transactions of this sort, we are dealing with two factors—with the demands of the organism for energy and with the efficiency with which these demands may be met by the fuel assimilated from the food or drawn from the tissues. The term “basal metabolic rate” when applied to the heat production of an animal under defined “basal” conditions is thus misleading if it is interpreted to mean the minimum rate of energy demand, and it is particularly confusing if used as a base when assessing the capacity of a foodstuff to provide the animal with the energy necessary to support its living processes—lack of appreciation of this point has resulted in a half a century of controversy.

The fact that foodstuffs differ in their ability to induce extra heat production in the animal organism was recognized early in the study of energy metabolism,

but the failure to realize that heat production is an incident, not an end, of metabolism, led, for a period, to the quite erroneous assumption that the function of a ration which would maintain a state of energy equilibrium in an animal at rest in a neutral thermal environment was merely to provide the energy necessary for the maintenance of body temperature. There is, however, ample evidence to show unequivocally that only a fraction of the combustible energy of a

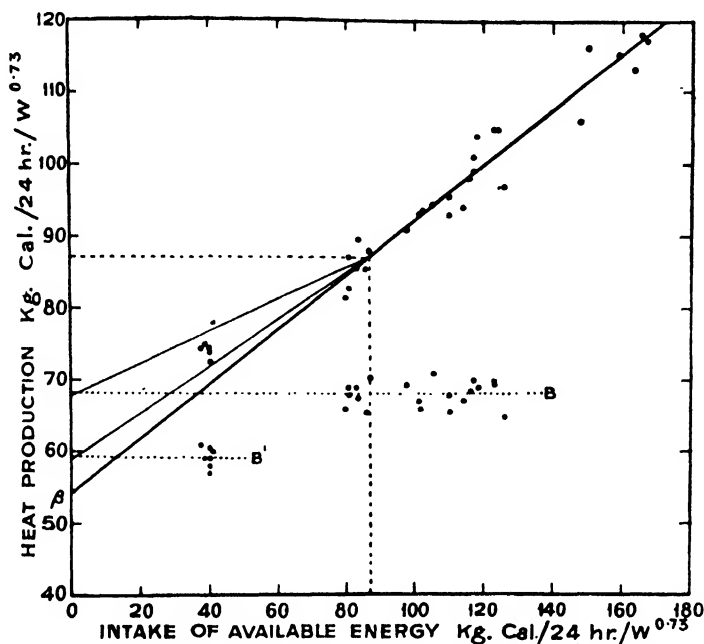


Fig. 4.—The relationship between the intake of available energy, I , from a fodder of constant composition, and the heat production, M , of sheep consuming it is plotted together with the “basal” fasting rate, B , and the inanition basal, B' . The available energy is the combustible energy of the fodder minus the sum of the combustible energy of the fodder minus the sum of the combustible energy of the faeces, urine and of the methane which is a product of fermentation in the rumen.

Above maintenance the heat produced by the animals is linearly related to the energy which becomes available from the rations. A constant proportion of the available energy—37 per cent. of it from this particular fodder—is dissipated as heat without performing any useful work in the organism. This fraction is defined as “the heat increment”. Extrapolation of the relationship to zero intake provides the term, β , which may be tentatively defined as “true basal heat production”. This is 20 per cent. less than B , the rate of heat production of the resting animal under “basal” conditions, and implies that the energy provided by fuel drawn from the tissues is subject to a heat increment of 20 per cent. Thus, below maintenance, the slope of the relationship between the heat production and the energy available from the ration, alters. In this range, it is made up of two factors, the heat increment of the fodder and the heat increment of the tissue substances drawn upon to make up the energy deficit.

maintenance ration contributes to the quota necessary to sustain life, and that the remainder merely adds to the heat production already sufficient to support body temperature.

The heat increment—that quota of the total energy available from a substance being metabolized which is dissipated as heat apparently without serving any useful purpose in metabolism—has been considered to vary with the level of feeding, for in the relationship between food intake and heat output, there is an apparent difference above and below the maintenance level. Below

maintenance, however, when the available energy of the fodder is insufficient to provide for the energy requirements of the animal, the heat increment should be considered to be made up of two variables—the heat increment of the fodder and the heat increment of the tissue substance being drawn upon to make up the net energy deficit—and so, if these differ, the capacity of the fodder to provide useful energy would appear to alter abruptly as soon as energy equilibrium is established.

To illustrate these points let us consider, very briefly, the relationship between heat production and the intake of available energy, of sheep fed different quantities of the same foodstuff. It might be well to recall that the determination of the heat production of the ruminant entails special problems as by far the greater proportion of the energy that becomes available to the animal from the

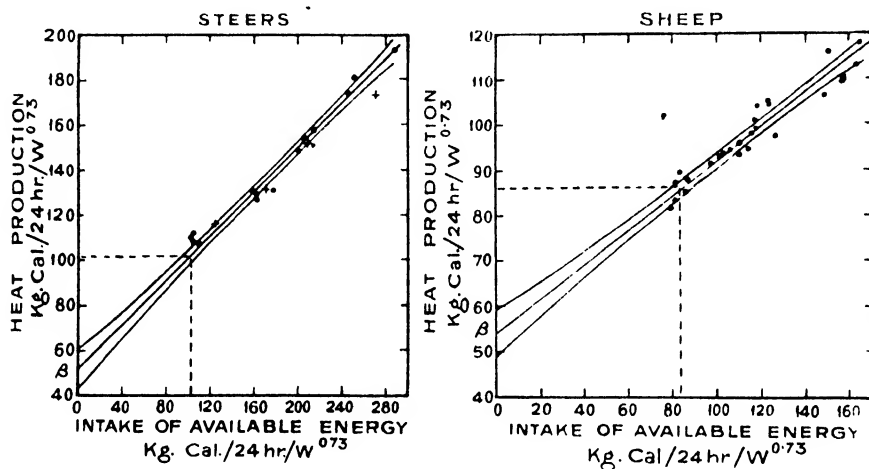


Fig. 5.—The apparent constancy of β , the point at which the linear relationship between heat production of an animal and the energy which becomes available to it from a fodder of constant composition, is illustrated by plotting two sets of independently observed data, one from observations on sheep and one from observations on cattle.

From the former, $\beta = 54.5$ Kg. Cal./ $W^{0.75}$ /24 hr. and from the latter $\beta = 51.8$ Kg. Cal./ $W^{0.75}$ /24 hr., the difference being well within the standard error of the observations.

β is tentatively defined as “true basal rate of heat production” for the convenience of assessing the relative heat increments of the available energy from various fodders. The term “basal” does not imply that β is a measure of the minimum expenditure of energy necessary to support the living processes, but, in distinction to its more general use to define the exogenous conditions under which heat production is estimated, it connotes in this expression an endogenous constant common to the metabolism of all foodstuffs.

carbohydrates in its fodder is derived from simple fatty acids produced by fermentation in the paunch. The chemical changes involved in the formation of these fatty acids through the activity of micro-flora are exothermic. The amount of heat dissipated during fermentation is approximately 6 per cent. of the combustible energy of the carbohydrates transformed. This quota of energy, like that of the heat increment, is valueless in the economy of the animal, other than when, in a cold environment, the amount of heat lost by radiation from the body surface is greater than that produced in the normal course of metabolism—under which circumstances, as a part of the overall heat increment, it spares, calorie for calorie, the energy that would be called upon merely to provide heat for the maintenance of body temperature. The heat production of the fed

ruminant is thus the sum of the heat produced as an end result of metabolic processes of the animal itself and the heat evolved by the fermentative activity of the microorganisms of its alimentary canal.

When the whole of the animal's energy requirement is drawn from the fodder, there is no reasonable doubt that *the relationship between intake of available energy and heat production is linear*. The heat increment quota is *thus a constant proportion of the available energy*—in this particular instance 37 per cent. of the available energy is dissipated as heat in the chemical work necessary to prepare the absorbed nutrients for their entry into the chain of events through which, according to the supply and demand, they may either be launched into the energy-producing cycles or laid down as body substance (Fig. 4).

Extrapolation of this linear relationship to the heat production axis should allow a close estimate to be made of the overall amount of energy spent on the physiological requirements of living, uninfluenced by the heat increment of the materials oxidized to provide this energy. Thus the intercept, β , which we might call tentatively the "true basal requirement", is less than B, the actual heat production under basal conditions (Fig. 4), by the heat increment of the fuel drawn from the body substance—which from this estimate is close to 20 per cent. of the total heat dissipated during fasting.

Theoretically, within the limits of the $W^{0.7}$ exponential relationship between metabolic rate and body weight, the value of β should be identical for all homeothermic animals. There is only one set of independent observations in the scientific literature that provides suitable data for testing this hypothesis—that gathered from a fine series of critically conceived and meticulously observed determinations of the heat output of bullocks fed at different planes on rations of identical composition (Fig. 5). The intercept, β , at which the extrapolated regression of the heat production: available energy relationship cuts the heat production axis in this case indicates a value 51.85 Kg. Cal./ $W^{0.7}/24$ hr. with a standard deviation of 3.38; the value of β derived similarly from experiments with the sheep is 54.56 Kg. Cal./ $W^{0.7}/24$ hr. with a standard deviation of 2.30. What then is implied in this apparently constant figure? We may be better prepared in our attempt to answer this question if we recall something of what is known of the transformations involving energy exchange that take place in the course of intermediary metabolism.

We can be sure that free energy is not liberated in one burst when substrates are oxidized within the cell. The abrupt gradient in the passage of electrons towards oxygen that such an event would imply is lessened by an ordered series of reactions, guided through the maze of thermodynamic possibilities by inter-linked specific catalysts that convey, by transphosphorylations, part of the free energy to compounds of relatively low molecular weight. From our present state of knowledge it appears not improbable that adenosine triphosphate assumes in this way the main role of carrier of energy within the cell, weaving between the sites where free energy is rendered available by respiration, and the sites where chemical work is to be done, bearing in the resonance of its pyrophosphate group a versatile means of energy exchange for the performance of work within the cell—one is tempted to consider this resonance energy to be universal currency in living matter.

During respiration within the cell, three steps are now known to be capable of intervening between the liberation of two hydrogen atoms from the substrate and their final combination with oxygen—the stages marked successively by reactions with the co-enzyme pyridine-nucleosides, which occur at E'_0 potentials about -0.32 v.; the reactions with the flavo-proteins, the protein complexes of d-ribityl 6 : 7 dimethyl-iso-alloxazine nucleoside, which occur about -0.6 v.; and the reactions with the iron-bearing cytochromes, which occur about $+0.39$ v.

A path such as this, in which each pair of electrons is intercepted three times at intervals during their journey between the substrate and oxygen, would impose a thermodynamic limit to the number of coupled reactions which could be brought about. Thus, if this path were traversed, the transphosphorylating

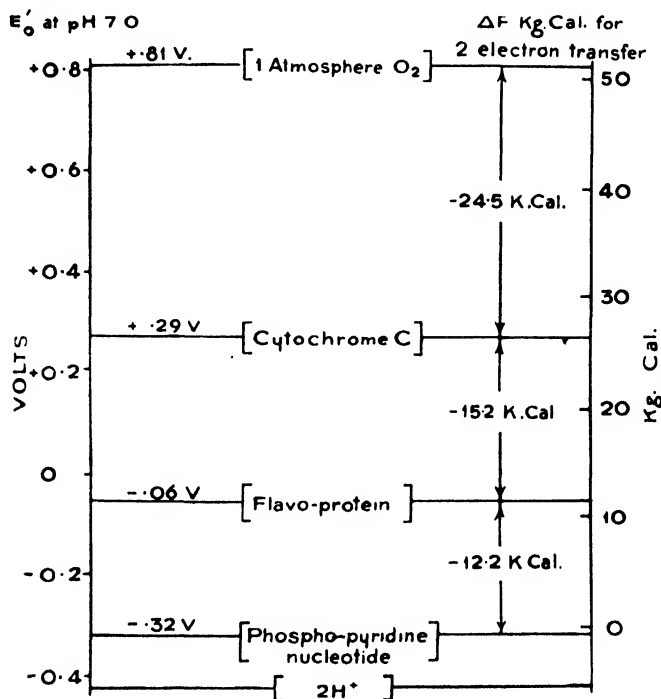


Fig. 6.—The free energy changes which would take place, when, during respiration within the cell, two electrons, set free by a dehydrogenating reaction, pass from the substrate, via phospho-pyridine nucleotide, flavo-protein and the cytochromes, to oxygen, may be assessed from the above figure.

The scale of oxidation-reduction potential E'_0 at pH 7.0, which is a measure of the free energy of the reactions involved, expresses, in volts, the difference of potential between the system at pH 7.0 and the normal hydrogen electrode (pH=0). The signs and the zero of this conventional scale are thus consequences of the mathematical convenience in the selection of the normal hydrogen electrode potential as a reference point. The chemical potential, i.e. the relative tendency for electron flow, of these reactions decreases progressively as the potential of oxygen is approached.

The scale of free energy changes is derived from the relationship, $-\Delta f = nF\Delta E$, in which Δf = the change in free energy in Joules, n = the number of electrons involved, F = the Faraday, and ΔE = the potential difference in volts.

As the average resonance energy in pyrophosphate bonds, $\sim P$, is close to 12 Kg. Cal./mole, which is equivalent to approximately 0.25 volt per two electron transfer, four coupled reactions, each involving the production of one $\sim P$, are the thermodynamic limit if the above course is taken, one in the 0.26v. interval between phospho-pyridine nucleotide and flavo-protein, one in the 0.33v. interval between flavo-protein and the cytochromes, and a possible two in the 0.52v. interval between the cytochromes and oxygen.

reactions which convert adenosine diphosphate to adenosine triphosphate and thereby convey 12 Kg. Cal./mole in the resonance of the added pyrophosphate group, would be limited to four, for each atom of oxygen consumed. Available evidence suggests that only three such transfers are achieved. This would imply the dissipation as heat of 30 per cent. of the free energy liberated by each

dehydrogenation—the remaining 70 per cent. being converted to resonance energy capable of performing work within the cell.

Some of you may recall that classical physiologists considered glucose “the preferred fuel” for the provision of energy to the organism. Let us, then, examine what is known of free energy changes which occur during oxidation of a glucose molecule within the cell. Glycolysis, you will agree, is now reasonably well understood to be a series of reversible reactions—extending in the animal organism between glycogen and pyruvic acid—through which glucose passes

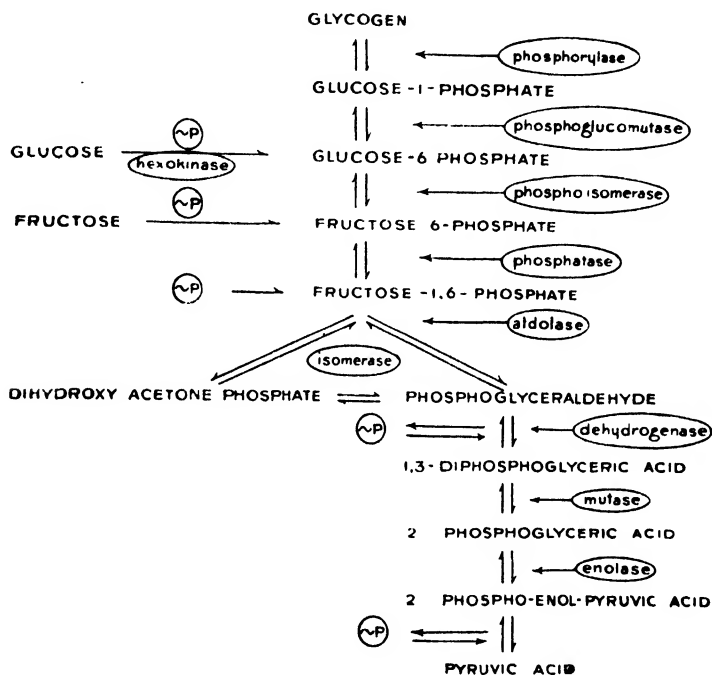


Fig. 7.—The probable course taken by glucose during glycolysis within animal tissues is indicated. The reactions between the links are reversible, the equilibria being influenced primarily by the concentration of adenosine triphosphate, the resonance energy of the pyrophosphate group of which is indicated by $\sim P$. Conversion of glucose to glucose-6-phosphate in which form it is introduced into the glycolytic chain involves the expenditure of one $\sim P$. The activity of hexokinase, which effects this priming reaction, is subject to hormonal control.

before its degradation product, pyruvic acid, enters the main energy-producing cycle where oxidation is completed. Admission of glucose into this chain of events necessitates its preliminary conversion to the Robinson ester, glucose-6-phosphate, by the intervention of the enzyme, hexokinase, and of adenosine triphosphate—a synthesis which entails the expenditure of 12 Kg. Cal./mole. from a pyrophosphate group to produce an ester-phosphate in which the resonance energy is in the vicinity of 3 Kg. Cal./mole. This priming reaction is thus exothermic and irreversible. Incidentally, the enzyme that affects it is now known to be subject to hormonal control—hexokinase activity is apparently poised between the inhibitory influences of anterior pituitary and adrenocortical hormones and the stimulatory influences of insulin.

Once glucose is introduced into the glycolytic chain as glucose-6-phosphate its conversion through the Cori ester, glucose-1-phosphate, to glycogen, or its

degradation via fructose-6-phosphate to the Harden-Young ester, fructose-1, 6 phosphate—by means of phosphatase and the intervention again of adenosine triphosphate, at this stage to convey a recoverable unit of 12 Kg. Cal./mole—hence via the triose, phosphoglyceraldehyde, by dehydrogenation to 1,3-diphosphoglyceric acid, and then in turn through 2-phosphoglyceric acid and phosphoenol-pyruvic acid to pyruvic acid, is apparently a matter of equilibria, influenced by the relative concentrations of the reacting links, and of the availability of adenosine triphosphate. The resonance energy of two pyro-phosphate groups of adenosine triphosphate are expended in this series of changes and four are recovered. Thus, during the degradation of a glucose unit from glycogen through these reactions to two molecules of pyruvic acid, recovery in terms of the energy transferred to pyrophosphate groups—i.e. in currency expendable on work within the cell—is approximately 35 per cent. of the energy set free. The overall recovery of energy from the glycolytic reactions if glucose itself is the starting point is further reduced to approximately 20 per cent. by the cost of the priming phosphorylation.* But the major part of the potential energy of the glucose molecule (83 per cent. of it) is retained in the two molecules of pyruvic acid. The overall cost, then, in preparing glucose for its excursion into the tricarboxylic acid cycle is about 14 per cent. of its combustible energy. While considering these reactions in some detail I have perhaps tried your patience, but in recalling them, my purpose is to stress that there are considerable expenses in terms of energy which must be met before even “the preferred fuel” is converted to a form in which it may be launched into the cycle which apparently is the main convertor of energy in the living cell.

The reactions of the tricarboxylic acid cycle which are now known—and which possibly are the more important ones—are no doubt familiar to you all, so I shall not try your patience further by discussing them in any detail. However, it might be well to bear in mind that the path taken by electrons liberated from some of the dehydrogenations in the respiratory cycle remains obscure. But once launched into this cycle, the 2-carbon fragment from all metabolites might be expected to yield the same amount of energy to phosphate bond resonance.

When discussing the coupled reactions that take place after electrons are liberated by dehydrogenation of the substrate, we concluded that the highest efficiency of energy transfer, which may be expected if the course suggested were taken, could not exceed 80 per cent. and that from experimental evidence available, which implies three transphosphorylations for each atom of oxygen consumed in the tricarboxylic acid cycle, the efficiency would probably be closer to 70 per cent. If this estimate is correct, oxidation of the two moles of pyruvic acid would transfer to adenosine diphosphate approximately 360 Kg. Cal. as resonance energy in pyrophosphate groups. Complete oxidation of a molecule of glucose, then, would yield in this currency close to 55 per cent. of the total free energy liberated—there is a net gain of 24 Kg. Cal./mole, it will be recalled, in the glycolytic reactions through which the glucose molecule is degraded to two molecules of pyruvic acid.† Thus it becomes evident that the net recovery of energy in a state capable of performing work within living tissues, falls far short of the total energy liberated during complete oxidation of a substrate.

* Conversion of one mole of glucose to two moles of pyruvic acid involves a free energy change of -115 Kg. Cal. As the resonance energy, $\sim P$, of the pyrophosphate group of adenosine triphosphate is approximately 12 Kg. Cal., the net recovery of energy in this currency is about 24 Kg. Cal.—the total recovery being $4\sim P$ and the expenditure $2\sim P$. The efficiency of the reaction in terms of resonance energy is thus approximately 20 per cent.

† Recovery of energy in the resonance of $\sim P$ (approx. 12 Kg. Cal./mole) on complete oxidation of a mole of glucose during respiration within the cell would be: from glycolysis, $2\sim P$; and from oxidation of the two moles of pyruvic acid arising from glycolysis, $30\sim P$, i.e., 384 Kg. Cal. from a total free energy change of 674 Kg. Cal.

Although fats take a course which, as yet, is not as well charted as the one taken by carbohydrates, their relatively low heat increment suggests that the higher fatty acids are launched into the reversible channels of metabolism with an efficiency comparable with that of glucose. Acetic acid—an important

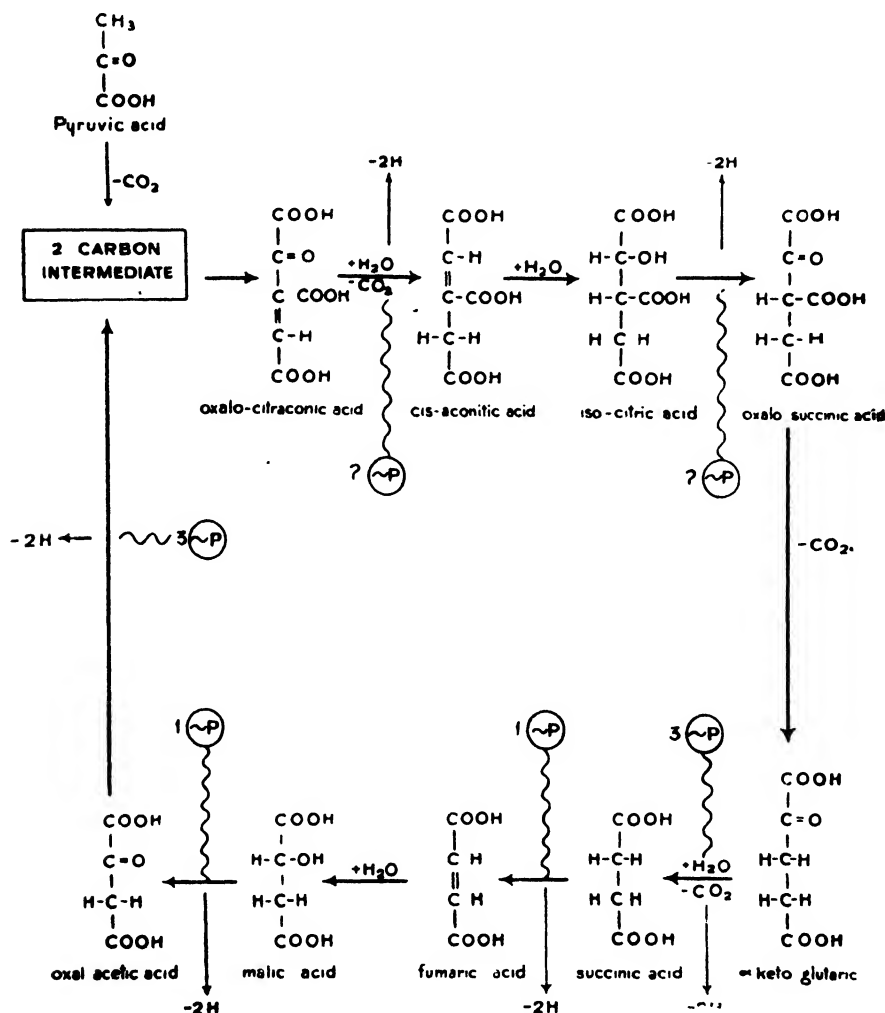


Fig. 8.—The known reactions of the tricarboxylic acid cycle through which respiratory dehydrogenation of many substrates is effected, are set out. Knowledge of these reactions has been achieved, for most part, from studies, *in vitro*, with tissue extracts and suspensions. The yield of $\sim\text{P}$ from the transphosphorylating reactions coupled to each stage of dehydrogenation is not yet clear. Experimental determination of the overall relationship between the amount of oxygen consumed and the yield of $\sim\text{P}$ during cellular respiration suggests that the production of $3\sim\text{P}$ is achieved at each stage. The thermodynamic limit would be $4\sim\text{P}$. (*vide* Fig. 6.)

fuel for ruminants—is apparently a much more expensive unit to launch into these channels, and for this reason is probably responsible for a major part of the relatively high rate of heat production in the fed ruminant. Propionic acid, which is formed along with acetic acid during fermentation of carbohydrates in the rumen, certainly has a materially smaller heat increment than that of acetic acid.

The heat increment of the available energy from protein is notoriously high. Here, however, we might expect the costs entailed in the formation and excretion of urea to be superimposed on the heat increments of the various fragments that arise from the deaminized amino acids, some of which take the metabolic course of the carbohydrates, some the course of the higher fatty acids, and some, like acetic acid, a much more expensive course. The costs of the chemical work necessary for the production of urea in the ornithine cycle, and for the osmotic work necessary for its excretion, must be discharged with the depreciated currency of resonance energy, and so are greater than those implied from the overall free energy change.

Hitherto I have refrained from employing the classical term "specific dynamic effect", which has been considered to be synonymous with "heat increment". I have avoided it because it implies that the increase of heat production which supervenes on the consumption of food is the result of a stimulus to metabolism—of an increase in the demands for energy by the tissues rather than a consequence of the costs entailed in the launching of the foodstuffs into channels through which these demands may be fulfilled. But the term and its implications may not lightly be dismissed when considering the effect that protein ingestion exerts on the heat production of animals, for it is conceivable that the dynamic equilibrium, which exists between the metabolic pool of amino acids and the tissue proteins, may be influenced by the amino acids arising from the ingested protein to an extent that might increase materially the expenditure of energy necessary to sustain protoplasmic structure.

Let us consider, very briefly, the energy transactions involved in this equilibrium, as they will serve, *inter alia*, to illustrate the relatively great losses of energy entailed in the performance of the chemical work in living tissues.

We have discussed the evidence which renders it probable that resonance energy of pyro-phosphate groups constitutes a most important currency for the performance of work in living tissues. The exchange rates for conversion of the energy liberated by respiration to this currency are obviously high, and—to continue the metaphor—its purchasing power in terms of chemical work is, more often than not, very low. For instance, the costs of synthesizing a peptid bond between two amino acids, which effects a free energy increase of about 3 Kg. Cal./mole, involves the expenditure of the whole of the resonance energy of the pyro-phosphate group of adenosine triphosphate, with the dissipation of 75 per cent. of it. Thus, synthesis of protein is a costly item in the economy of the organism; its efficiency in terms of the "preferred fuel" would not exceed 14 per cent., and, in terms of the fuel absorbed from the intestinal tract of ruminants, would be reduced further by the heavy losses involved in the high heat increment. A considerable amount of energy is clearly necessary to maintain the structure of protoplasm, for there is no doubt that the proteins in living cells are in constant flux and that their apparent steady state is but a reflexion of the relative rates of their degradation and resynthesis. From experiments in which N^{15} -tagged amino acids were fed to humans and to rats there is eloquent evidence to indicate that the rate of protein turnover within the tissues of a homeothermic animal in a steady nutritional state, varies with the size of the animal. The ratio of the rates of protein synthesis per unit weight of the rat and of Man, estimated by this means, is very close to 5 : 1—practically identical with the relative rates of energy expenditure under basal conditions. We have already concluded (Table 1) that the heat production within the liver accounts for over 30 per cent. of the total heat production of Man under basal conditions. The rate of protein turnover in the liver of Man, assessed from the rate of loss of N^{15} from the blood-plasma proteins, which there is good reason to believe are produced in the liver and are in dynamic equilibrium with the liver

protoplasmic proteins, bears a similar relationship to the overall rate of protein turnover. And the comparatively slow rate of protein turnover in the muscles is closely parallel to their basal heat production.

These relationships can hardly be fortuitous. They suggest that the mechanism which poises the basal rate of heat production might operate by influencing the rate of protein turnover. But, in so far as the latter may be estimated from exchange reactions, the energy cost of the syntheses necessary to preserve the tissue proteins in a steady state is not of the same order as the energy dissipation implied by the total heat production, even when the depreciated rate of the currency which effects these syntheses is accounted for. Nevertheless a common factor is suggested and we are impelled to seek it, for knowledge of the mechanism involved would greatly clarify the central problem of energy metabolism. Although many suggestive clues are available, no satisfactory explanation of the mechanism through which the rate of heat production is poised in homeothermic animals emerges from our present state of knowledge. It is not yet clear whether the nervous and hormonal agencies primarily responsible for the overall rate of heat production in the resting animal, exert their influence by altering the demands of the tissues for energy, or by altering the capacity of the fuel to meet these demands. The former influence could operate by controlling the relative rates of the hydrolyses and syntheses which determine the dynamic state of protoplasmic constituents. The latter could operate by controlling the series of equilibria between the links of the chain of intermediary metabolic events through which the universal currency of resonance energy is produced. Direct hydrolysis of adenosine triphosphate, by phosphatase, with the dissipation of its resonance energy without performance of chemical work could, in this way, alter very materially the rate of fuel consumption.

In both of these effects enzyme systems would be involved, and there is, already, unequivocal evidence in the case of hexokinase that some at least of the known hormones exert their profound physiological effects by influencing the activity of specific enzymes.

We might speculate without end, and progress little without experimental evidence, however, and we must leave this question unanswered, along with many of the others which have confronted us during our somewhat superficial survey of energy metabolism. But, the course towards the solution of some at least of the problems which have intrigued physiologists for more than a century is now clear enough to invite the curious: and it is perhaps not too much to expect that a great clarification of our knowledge of energy transactions in living matter will soon be achieved.

In our excursion this evening, we have failed to discover any clue which might help explain the high rate of energy dissipation that occurs in the brain. We may, however, be reasonably sure that this expenditure is not directly concerned with the elaboration of that tenuous secretion, thought. We may thus take heart, for this final product of the ephemeral turbulence in the universal flow towards maximum entropy apparently calls for extremely little expenditure of energy.

Gentlemen, I thank you for your attention. If I have provoked rather than diverted you, my task is fulfilled, for I have attempted to carry out the reference set down by Archibald Liversidge and conveyed to me in your invitation.

HALOGENOSTANNATES (IV) OF SOME COMPLEX CATIONS.

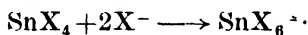
By J. R. ANDERSON, A.S.T.C.,
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Manuscript received, November 8, 1950. Read, December 6, 1950.

Tin in the oxidation state of +4 is characterized by forming compounds with halogens of the type SnX_4 and SnX_6^- . Compounds of SnX_4 that have been examined have a tetrahedral structure and are presumably using sp^3 bonds. For salts containing the SnCl_6^- ion the octahedral arrangement has been confirmed for the K, Rb, Cs, NH_4 and Tl compounds (Wells, 1945).

Octahedral bonds from an element such as tin differ from those which occur in a complex such as PtCl_6^- . This ion has d^2sp^3 orbitals available and these after hybridization give bonds of nearly maximum strength. Octahedral d^2sp^3 bonds for Sn involves the use of d orbitals with the same principal quantum number as the s and p orbitals (Kimball, 1939). From the observed values of interatomic distances in SnCl_6^- Pauling (1944) has assigned the octahedral bonds to the $5s\ 5p^3\ 5d^2$ orbitals, use being made of the unstable 5d orbitals of the valence shell itself.

The formation of the hexahalogenostannate ion takes place by reaction of the SnX_4 molecule with excess halide ions



The reaction appears to take place more readily and the compounds formed are more stable with the increasing electronegativity of the halogen. Thus the fluoro and chloro-stannate ions are well defined and numerous compounds are known (Mellor, 1927), but the bromo and iodo-stannates are not so well characterized.

In this investigation we have prepared some chlorostannates and bromostannates of complex cobalt cations and two iodostannates of complex ferrous ions. These are listed below:

- I. Tris(ethylenediamine) cobalt (III) bromide bromostannate (IV), 1-hydrate
- II. Trans-dibromo-bis-(ethylenediamine) cobalt (III) chlorostannate (IV)
- III. Trans-dibromo-bis-(ethylenediamine) cobalt (III) bromostannate (IV)
- IV. Tris(1 : 10 phenanthroline) iron (II) iodostannate (IV)
- V. Tris(22' dipyridyl) iron (II) iodostannate (IV).

They are all well defined, coloured, crystalline substances sparingly soluble, but completely hydrolysed in hot water. Analogous types of compounds to I, II and III have been previously reported: $[\text{Co en}_3]\text{Cl}.\text{SnCl}_6.2\text{H}_2\text{O}$ (McCutcheon and d'Ouville, 1947) $[\text{Co en}_2\text{Cl}_2]_2\text{SnCl}_6$ (Spacu and Spacu, 1931), $[\text{Co en}_2\text{Cl}_2]_2\text{SnBr}_6$ (Spacu and Spacu, 1932). We have repeated the preparation of these compounds in order to compare them with the above. In contact with cold water, it was found that the bromo-stannates decomposed more rapidly than the corresponding chlorostannates, also decomposition was more rapid with

compounds containing the cation $[\text{Co en}_3]^{+++}$ than with corresponding halogenostannates containing $[\text{Co en}_2\text{X}_2]^+$ (En =ethylenediamine, $\text{X}=\text{Cl}$, Br). The iodostannates IV and V did not appear to hydrolyse to any extent in cold water, probably due to their insolubility. The only compounds containing the SnI_6^- ion so far reported are Cs_2SnI_6 , Rb_2SnI_6 and $[(\text{CH}_3)_4\text{As}]_2\text{SnI}_6$, prepared by Auger and Karantassis (1925).

EXPERIMENTAL.

I. *Tris(ethylenediamine) cobalt (III) bromide bromostannate (IV)—1-hydrate.*

$[\text{Co en}_3]\text{Br}_3$ was prepared by a similar method to that given for $[\text{Co en}_3]\text{Cl}_3$ (Fernelius, 1946). The product was dried at 120°C .

Found : Br, 50.05%.

Calculated for $[\text{Co en}_3]\text{Br}_3$: Br, 50.07%.

Tris(ethylenediamine) cobalt (III) carbonate, prepared from $[\text{Co en}_3]\text{Br}_3$ and Ag_2CO_3 , was added slowly to a concentrated aqueous solution of $\text{H}_2\text{SnBr}_6 \cdot 8\text{H}_2\text{O}$ and the mixture warmed. Product was washed with ice cold HBr and dried at 110°C . No further loss in weight occurred after drying over P_2O_5 .

Found : Sn, 12.5% ; Br, 59.6% ; N, 9.05%.

$[\text{Co en}_3]\text{BrSnBr}_5 \cdot \text{H}_2\text{O}$ requires : Sn, 12.69% ; Br, 59.81% ; N, 8.99%.

The orange tetragonal crystals are immediately hydrolysed in cold water to SnO_2 hydrate. The compound cannot be recrystallised from HBr ; it dissolves in HBr (5 g. requires 80 ml. boiling 48% HBr) and yields $[\text{Co en}_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$ on cooling.

Found : Br, 45.5%.

Calculated : Br, 45.0%.

II. *Trans-dibromo-bis(ethylenediamine) cobalt (III) chlorostannate (IV).*

Trans $[\text{Co en}_2\text{Br}_2]\text{Br} \cdot \text{HBr}$ was prepared by treating aqueous trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ with Ag_2O , filtering and evaporating the filtrate to dryness with HBr (Mellor, 1935).

Found : Br, 63.65%.

Calculated for $[\text{Co en}_2\text{Br}_2]\text{Br} \cdot \text{HBr}$: Br, 63.96%.

An aqueous solution of trans $[\text{Co en}_2\text{Br}_2]\text{Br} \cdot \text{HBr}$ was added to a solution of H_2SnCl_6 in concentrated HCl and warmed on a water bath. On cooling, bright green perfectly formed rhomb shaped crystals were deposited. These were washed with HCl and dried at 110°C .

Found : Sn, 11.7% ; Br, 32.8% ; Cl, 20.2% ; Co, 11.4%.

$[\text{Co en}_2\text{Br}_2]_2\text{SnCl}_6$ requires : Sn, 11.76% ; Br, 31.67% ; Cl, 21.08% ; Co, 11.68%.

Hydrolysis in cold water is slow ($\frac{1}{4}$ – $\frac{1}{2}$ hour); the compound is soluble in 10% aqueous solution of H_2SnCl_6 from which it crystallizes on cooling.

III. *Trans-dibromo-bis(ethylenediamine) cobalt (III) bromostannate (IV).*

$[\text{Co en}_2\text{CO}_3]_2\text{CO}_3$ (reddish violet) was prepared by heating an aqueous solution of trans $[\text{Co en}_2\text{Cl}_2]\text{Cl}$ with Ag_2CO_3 —cf. Mellor, *Inorg. and Theor. Chem.*, 14, 819—filtering and concentrating the filtrate. Titration with cold standard HCl gave an equivalent weight of 268; one replaceable CO_3 group requires equivalent weight of 269.2.

$[\text{Co en}_2\text{CO}_3]_2\text{CO}_3$ was added to an excess of $\text{H}_2\text{SnBr}_6 \cdot 8\text{H}_2\text{O}$ dissolved in a minimum quantity of 48% HBr . At first the mixture remained reddish violet (cis form) (Mellor, 1935), but on heating on a water bath for ten minutes the product became yellowish green (trans form). The compound was washed with HBr and dried at 110°C .

Found : Sn, 9.2% ; Br, 62.0% ; N, 8.62% ; Co, 8.75%.

$[\text{Co en}_2\text{Br}_2]_2\text{SnBr}_6$ requires : Sn, 9.31% ; Br, 62.62% ; N, 8.78% ; Co, 9.24%.

Recrystallization from HBr (1 g. requires 60 ml. boiling HBr) is accompanied by a small amount of decomposition.

Found : Sn, 8.6% ; Br, 61.0%.

The bright yellowish green cubes and prisms decompose in cold water, yielding SnO_2 hydrate, somewhat more rapidly than the chlorostannate.

IV. *Tris(1 : 10) phenanthroline iron (II) iodostannate (IV).*

Tris(1 : 10 phenanthroline) iron (II) iodide 1-hydrate was prepared from 1 : 10 phenanthroline 1-hydrate (m.pt. 99°C .), $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, and KI in aqueous solution and recrystallized from water.

Found : N, 9.84% ; H_2O , 2.14%.

Calculated for $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{I}_2 \cdot \text{H}_2\text{O}$: N, 9.68% ; H_2O , 2.08%.

1.0 g. $[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{I}_2 \cdot \text{H}_2\text{O}$ was dissolved in methanol and added slowly, with stirring, to a methanol solution containing 0.75 g. SnI_4 and 3 ml. 66% HI. The mixture was warmed to 50°C ., stood half an hour, cooled in ice, then filtered, washed well with methanol and dried at 110°C . The product consisted of dark red prisms. Yield, 1.40 g.

Found : Sn, 8.0% ; I, 51.6% ; N, 5.77%.

$[\text{Fe}(\text{C}_{12}\text{H}_8\text{N}_2)_3]\text{SnI}_6$ requires : Sn, 8.04% ; I, 51.56% ; N, 5.69%.

Attempts to prepare this compound, using NaI in place of HI, failed. Products were obtained which gave reproducible analysis figures, in which the N : I ratio was 1 : 1 but the tin content was high.

Found : Fe, 3.35, 3.30% ; N, 5.07, 5.16% ; Sn, 8.7, 8.7% ; I, 46.5%. This gives Fe : N : Sn : I = 0.985 : 6.00 : 1.20 : 6.00.

Hence it appears that the presence of HI in the methanol solution is necessary to stabilize the SnI_6^{2-} ion ; sodium iodide is unable to prevent some of the SnI_6^{2-} being converted to SnO_2 .

V. *Tris(2,2' dipyridyl) iron (II) iodostannate.*

1 g. of tris(2,2' dipyridyl) iron (II) iodide dissolved in methanol was slowly added to a methanol solution containing 0.81 g. SnI_4 and 2-3 ml. 66% HI. After warming to 50°C . and cooling, the reddish black crystals were washed with methanol and dried at 110°C . Yield : 1.25 g.

Found : N, 6.15% ; I, 53.6%.

$[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]\text{SnI}_6$ requires : N, 5.98 ; I, 54.20%.

As with the 1 : 10 phenanthroline compound when NaI was used in place of HI, a product was obtained in which the percentage of tin was high.

Found : N, 5.10% ; Sn, 9.5, 9.5% ; I, 49.0%, i.e. N : Sn : I = 5.50 : 1.24 : 6.00.

SUMMARY.

The chlorostannate and bromostannate of the complex cation $[\text{Co en}_2\text{Br}_2]^+$, the bromostannate of $[\text{Co en}_3]^{+++}$ and iodostannates of $[\text{Fe}(\text{open})_3]^{++}$ and $[\text{Fe}(\text{dipy})_3]^{++}$ have been prepared as well-defined coloured crystalline compounds (en = ethylenediamine ; open = 1 : 10 phenanthroline ; dipy = 2,2' dipyridyl). With the trivalent cation $[\text{Co en}_3]^{+++}$ only a compound containing a mixed anion—bromide + bromostannate—could be obtained. The analogous chlorostannate is similar. All the compounds are completely hydrolysed in hot water. In cold water, the bromostannates decompose more readily than the corresponding chlorostannates.

ACKNOWLEDGEMENT.

The authors are indebted to Dr. F. P. J. Dwyer for his interest and help and for supplying the tris (dipyridyl) ferrous iodide, also to Mr. E. R. Cole for the nitrogen analyses.

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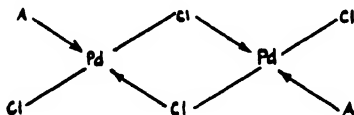
PALLADIUM COMPLEXES.

PART II. BRIDGED COMPOUNDS OF PALLADIUM WITH o-METHYL-MERCAPTobenzoic ACID.

By S. E. LIVINGSTONE, A.S.T.C.,
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Mann and Purdie (1935, 1936) prepared bridged compounds of palladium with trialkyl phosphines and arsines of the type



where $A = (C_4H_9)_3P$ and $(C_4H_9)_3As$.

These were prepared by the action of ammonium chloropalladate (II) on the dichloro-bis(tributyl-phosphine or arsine) palladium (II) compounds. They reported difficulty with the corresponding reaction using the dialkyl sulphide compound. Mann and Wells (1938) by X-ray examination showed that the trimethyl-arsine analogue had the trans structure. They also prepared similar compounds with $-Br$, $-NO_2$, and $-SCN$ in place of $-Cl$ in the bridging positions.

As part of the systematic examination of the bridged compounds prepared by Mann *et al.*, Chatt and Mann (1939) reported that compounds in which the two arsine groups were contained in a chelate molecule did not react with ammonium chloropalladate (II) to form bridged complexes.

In the previous communication (Livingstone, Plowman and Sorenson, 1951), it was reported that o-methyl-mercaptobenzoic acid functioned as a chelate group and formed with palladium the compound bis(o-methyl-mercaptobenzoato) palladium (II), I. Potassium chloropalladate (II) solution added to the solution of I produced II from which the two molecules of water were expelled at a temperature just below decomposition. If, on the other hand, the procedure was reversed and a solution of I was added to potassium chloropalladate (II) solution the product III was anhydrous. Moreover, II consisted of deep orange tetragonal prisms of m.pt. $214^\circ C.$, while the yellowish brown tetragonal prisms of III had a m.pt. of $224^\circ C.$

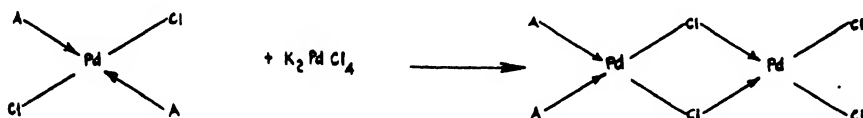
The empirical formulæ of these compounds are $(C_8H_7O_2S)_2PdCl \cdot H_2O$ and $(C_8H_7O_2S)_2PdCl$ respectively. It is almost certain that these compounds are dimeric (Mann and Wells, 1938), but they are insoluble in organic solvents and the molecular weights were not determined.

Assuming that the compounds are dimeric, there appears to be no alternative formulation of III in which one chelate group is attached to each palladium atom.

This substantiates that the formation of the bridged compounds prepared by Mann and his co-workers takes place thus :



and not



There remains to consider the relationship between II and III. The possibilities appear to be limited to

- (i) dimorphous forms ;
- (ii) alternate formulation of II ;
- (iii) structural isomers.

Both II and III are precipitated from boiling aqueous solution which appears to obviate the possibility of dimorphous forms. Alternate formulations of II are possible involving Pd-OH bonds and free carboxylic acid groups. Finally, since the compounds contain two asymmetrical sulphur atoms, they may be related as racemic and meso forms. On the limited amount of data obtained it is impossible to decide which formulation is correct.

The compound II was also prepared by the slow addition (one week) of a dilute aqueous solution of the sodium salt of *o*-methyl-mercaptobenzoic acid to a large excess of an ice-cold solution of K_2PdCl_4 . Thus the bridged compound was formed directly from the chelating acid without first precipitating out bis(*o*-methyl-mercaptobenzoato) palladium (II).

Although practically insoluble in water and organic solvents, the bridged compound II dissolved in sodium hydroxide solution, three equivalents being required per mole of bridged compound. Acidification of this solution with two equivalents of hydrochloric acid precipitated reddish brown crystals of a new compound, IV, which has been formulated as containing mixed bridging atoms.

A saturated aqueous solution of II which was only very sparingly soluble in water was found to have a pH of 4.5-4.8, indicating that considerable hydrolysis had taken place, possibly as given in Table 2. A suggested mechanism of the reaction of II with sodium hydroxide is given in Table 3. Compound II was found to be soluble in a concentrated solution of potassium chloride (cf. Chatt and Mann, 1939). However, no compound was isolated from the solution.

Heating of II with dilute hydrochloric acid yielded bis (*o*-methyl-mercaptobenzoic acid) palladium (II), V (Livingstone, Plowman and Sorenson, 1951). A 0.00025 M solution of V was found to have a pH of 3.6 ; this is the same pH value as hydrochloric acid of the same concentration. This confirms that the reaction, as given in Table 4, takes place in solution, since recrystallization of V from water yields VI (Livingstone, Plowman and Sorenson, 1951).

A bridged compound VII similar to III, but with bromine atoms in place of the chlorine, was prepared by a similar method to that used for III.

TABLE 1

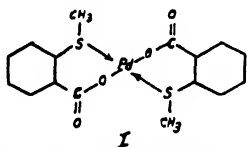
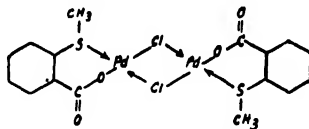
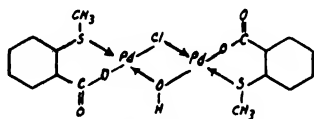
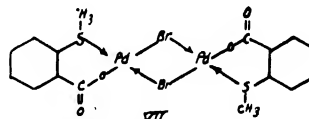
*Bis(o-methyl-mercaptobenzoato) palladium (II)**II Bis(o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II), 2-hydrate**III Bis(o-methyl-mercaptobenzoato)-μ-dichloro-dipalladium (II)**Bis(o-methyl-mercaptobenzoato)-μ-monohydroxo-monochloro-dipalladium (II)**Bis(o-methyl-mercaptobenzoato)-μ-dibromo-dipalladium (II)*

TABLE 2

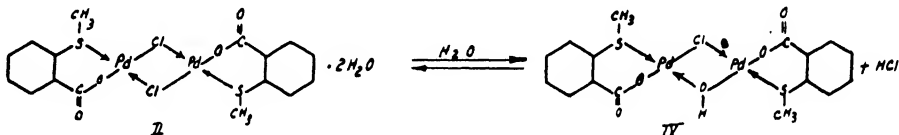


TABLE 3

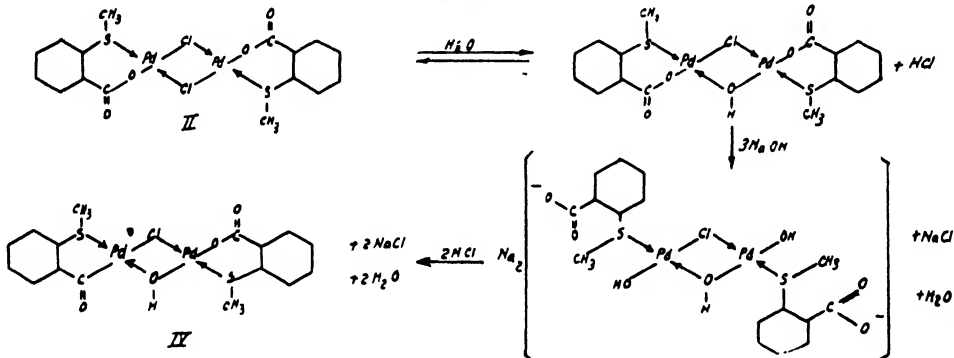
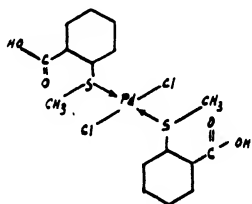
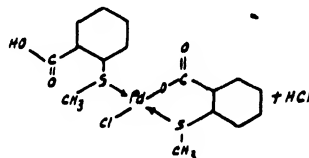


TABLE 4

*Dichloro-bis(o-methyl-mercaptobenzoic acid)-palladium (II)**Monochloro-bis(o-methyl-mercaptobenzoato)-palladium (II)*

On substituting trans-dichlorodiammine palladium (II), trans-diglycine palladium (II) (Pinkard, Sharratt, Wardlaw and Cox, 1934), bis (anthranilato) palladium (II) VIII, and bis(o-carboxy-phenyldimethylarsine) palladium (II) IX, in place of bis(o-methylmercapto-benzoato) palladium (II) I, no reaction with potassium chloropalladate (II) to form bridged compounds was observed. Mann and Purdie (1935) were able to prepare bridged palladium compounds with dichloro-bis(trialkyl-phosphine) palladium (II) and dichloro-bis (trialkyl-arsine) palladium (II) but not with the corresponding sulphur analogues. From these results it seems that the formation of μ -halogeno compounds of palladium is dependent on the nature of the attached ligand.

EXPERIMENTAL.

I. *Bis(o-methyl-mercaptobenzoato) palladium (II)*.

Prepared by the reaction of potassium chloropalladate (II) on sodium o-methyl-mercapto-benzoate (Livingstone, Plowman and Sorenson, 1951). A 0.0025 M solution of the compound was found to have a pH of 4.2.

II. *Bis(o-methyl-mercaptobenzoato)- μ -dichloro-dipalladium (II) 2-hydrate*.

(a) To a solution of bis (o-methyl-mercaptobenzoato) palladium (II) (1 g.) in boiling water (180 ml.) was added, drop by drop over thirty minutes, an aqueous solution (40 ml.) of potassium chloropalladate (II) (0.97 g.). After twenty minutes at the boiling point crystals began to form. The deep orange tetragonal prisms were almost insoluble in hot water, only very slightly soluble in boiling alcohol, but insoluble in organic solvents. Yield 1.1 g.; m.pt. 214° C.

When the compound, dried over P_2O_5 , was heated in a closed tube, water was evolved at a temperature just below the melting point.

Found: Pd, 32.6%; Cl, 10.8%.

(b) An aqueous solution (90 ml.) of sodium o-methyl-mercaptobenzoate (2.3 g.) was added very slowly from a burette to an ice cold solution (270 ml.) of potassium chloropalladate (II) (15.6 g.). After six hours crystallization commenced; the total addition took six days. The product, washed with water and dried over P_2O_5 , consisted of deep orange tetragonal prisms, m.pt. 214° C.; water evolved when heated to just below the melting point.

Found: Pd, 32.6%; Cl, 10.8%.

$[(C_8H_7O_2S)PdCl]_2 \cdot 2H_2O$ requires: Pd, 32.60%; Cl, 10.83%.

III. *Bis(o-methyl-mercaptobenzoato)- μ -dichloro-dipalladium (II)*.

To an aqueous solution (50 ml.) of potassium chloropalladate (II) (0.48 g.) was added slowly (20 min.) at the boiling point an aqueous solution (90 ml.) of bis(o-methyl-mercaptobenzoato) palladium (II) (0.5 g.). After ten minutes heating crystallization commenced. Yield 0.58 g. The product, washed with water and dried over P_2O_5 , consisted of pale yellowish brown prisms of m.pt. 224° C. No water was evolved on heating to decomposition.

Found: Pd, 34.2%; Cl, 10.9%.

$[(C_8H_7O_2S)PdCl]_2$ requires: Pd, 34.49%; Cl, 11.46%.

IV. *Bis(o-methyl-mercaptobenzoato)- μ -monohydroxo-monochloro-dipalladium (II)*.

Bis(o-methyl-mercaptobenzoato)- μ -dichloro-dipalladium (II) 2-hydrate II (1.00 g.) was treated with 0.1 N NaOH solution. It required 42.3 ml. 0.1085 N NaOH to dissolve completely (i.e., exactly three moles of NaOH to two moles of Pd). To this solution was added 28.0 ml. 0.1089 N HCl (i.e. two moles HCl to two moles of Pd). An amorphous brown precipitate formed, which, on standing overnight, crystallized into small reddish brown crystals which appeared to be cubic. Yield, 0.68 g.

Found: Pd, 35.0%; Cl, 6.0%.

$(C_8H_7O_2S)_2Pd_2OHCl$ requires: Pd, 35.55%; Cl, 5.98%.

V. *Dichloro-bis(o-methyl-mercaptobenzoic acid) palladium (II)*.

(a) A sodium hydroxide solution of bis (o-methyl-mercaptobenzoato)- μ -dichloro-dipalladium (II) 2-hydrate II (0.7 g.) was treated with excess hydrochloric acid (2 N) and reddish brown crystals were deposited, m.pt. 250° C.

Found: Pd, 20.8%; Cl, 13.7%.

Calculated for $(C_8H_7O_2S)_2PdCl_2 \cdot 2H_2O$: Pd, 20.76%; Cl, 13.80%.

The product could be recrystallized by digesting the mother liquor to yield reddish brown pyritohedra of m.pt. 250° C.

(b) On treating II with hydrochloric acid (2 N) and digesting for half an hour at the boiling point, reddish brown crystals were obtained, m.pt. 250° C.

Found: Pd, 21.0%.

A 0.00025 M solution was found to have a pH of 3.6.

VII. *Bis(o-methyl-mercaptobenzoato)- μ -dibromo-dipalladium (II)*.

To a boiling aqueous solution (100 ml.) containing potassium bromopalladate (II) (1 g.) and potassium bromide (0.5 g.) was added a hot aqueous solution (200 ml.) of bis (o-methyl-mercaptobenzoato) palladium (II) (0.75 g.) over a period of 15 minutes. After 10 minutes crystals began to form; after a further 15 minutes heating the red brown crystals were filtered hot, washed with hot alcohol, then acetone. Yield 0.85 g.

Found: Pd, 30.3%; Br, 22.6%.

$[(C_8H_7O_2S)_2PdBr]_2$ requires: Pd, 30.16%; Br, 22.59%.

VIII. *Bis(anthranilato) palladium (II)*.

The reaction of anthranilic acid with Pd^{II} has been investigated by Sheintais (1939), who determined the sensitivity, but apparently did not characterize the compound.

Anthranilic acid (5.5 g.) was dissolved in aqueous sodium hydroxide solution (1.6 g. NaOH) and a solution of potassium chloropalladate (II) (6.5 g.) added in the cold. The yellow crystalline product was washed with water and acetone and dried, m.pt. 245° C.

Found: Pd, 27.8%; N, 7.39%

$Pd(C_8H_6O_2N)_2$ requires: Pd, 28.16%; N, 7.39%

IX. *Bis(o-carboxy-phenyl-dimethylarsine) palladium (II) 2-hydrate*.

o-Carboxy-phenyl-dimethylarsine (1.20 g.)—prepared by the method of Barclay and Nyholm (1947)—was dissolved in one equivalent of sodium hydroxide solution (30 ml.) and a solution (10 ml.) of potassium chloropalladate (II) (1.25 g.) added. The mixture was warmed for five minutes, then cooled. The yellow product was washed with water and recrystallized from water, m.pt. 178° C. When the compound, dried over P_2O_5 , was heated, water was given off at a temperature just below decomposition.

Found: Pd, 18.15%; C, 36.34%; H, 3.94%.

$Pd(C_8H_9O_2As)_2 \cdot 2H_2O$ requires: Pd, 18.00%; C, 36.47%; H, 4.08%.

SUMMARY.

Further investigations of the reactions of compounds of o-methyl-mercaptobenzoic acid with divalent palladium have shown that it is possible to prepare bridged halogeno compounds containing o-methyl-mercaptobenzoic acid as a chelating molecule. The μ -dichloro compound $[C_8H_7O_2SPdCl]_2$ was found to exist in two forms, with different colours and melting points, one anhydrous and the other hydrated. A corresponding dibromo analogue $[C_8H_7O_2SPdBr]_2$ was prepared in the anhydrous form. One of the chloro atoms in the μ -dichloro compound was replaceable by a hydroxo group to give a new complex $(C_8H_7O_2S)_2Pd_2OHCl$, containing mixed bridging groups. Various reactions of these compounds are discussed. Similar μ -halogeno compounds were not obtained with certain other ligands attached to the palladium.

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THE CHEMISTRY OF OSMIUM.

PART VIII. A NOTE ON THE PREPARATION OF AMMONIUM HEXACHLOROSMATE IV.

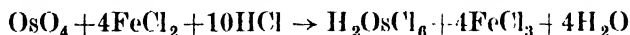
By F. P. DWYER, D.Sc.,
and J. W. HOGARTH, A.S.T.C.

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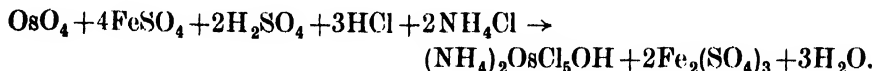
The alkali metal hexachlorosmates IV R_2OsCl_6 can be prepared by heating osmium tetroxide with hydrochloric acid. Chlorine is liberated slowly, some of the volatile tetroxide is lost and the acid H_2OsCl_6 results. A better method (Wintrebert, 1903) involves the formation of osmyl-oxy nitrite by reaction between the tetroxide and potassium nitrite. This substance, on addition to boiling hydrochloric acid, gives the potassium salt. Despite the claims of Wintrebert, the yield of potassium hexachlorosmate is never more than 40–50 per cent., reckoned on the weight of tetroxide used. The main source of the loss appears to be in the simultaneous formation of the very soluble potassium penta-nitro osmate III, with the osmyl-oxy nitrite.

Further, the decomposition of potassium osmyl-oxy nitrite is uncertain, the best results being obtained by the very slow addition of the substance to vigorously boiling acid.

Since the redox potential of the Os^{III}/Os^{IV} system in hydrochloric acid is 0.532 volt (Dwyer, Humpoletz and Nyholm, 1947), it can be concluded that ferrous salts should reduce osmium tetroxide in hydrochloric acid to the tetravalent stage and no further. When the reaction was carried out with ferrous chloride in concentrated hydrochloric acid, a deep orange solution of the acid H_2OsCl_6 resulted. Addition of ammonium chloride then gave an almost quantitative yield of analytically pure ammonium hexachlorosmate IV.



The alkali metal pentachlor-hydroxy osmates IV, $R_2[OsCl_5OH]$, were prepared by Krauss and Wilken (1924) from hydroxy-trichloro osmium IV. This series of complex salts can be obtained by reduction of osmium tetroxide with ferrous salts in controlled hydrogen and chloride ion concentrations. Although the reaction appeared to proceed quantitatively, the final yield was 30 per cent. of the theoretical, owing to the solubility of these complex salts, and the difficulty of removing ferrous and ferric salts. Only a trace of hexachlorosmate was formed. The pentachlor-hydroxy compounds are not intermediates in the formation of the hexachlorosmates. The ammonium salt $(NH_4)_2OsCl_5.OH$ could be boiled with concentrated hydrochloric acid in the presence of ammonium chloride without any ammonium hexachlorosmate resulting. This behaviour is similar to the ruthenium compounds $R_2[RuCl_5.OH]$, and confirms the observations of Mellor (1943) and Dwyer and Gibson (1950) on the hydrolysis of the hexachlorosmates.



EXPERIMENTAL.

Ammonium Hexachlorosmate IV.

Osmium tetroxide (1.0 g.) was heated with a mixture of ferrous chloride hexahydrate (10g.) and concentrated hydrochloric acid (30 ml.) in a stoppered flask on a water bath for 2 hours, with occasional shaking. The tetroxide rapidly dissolved and the deep greenish coloured solution became orange red. Ammonium chloride solution (20%—10 ml.) was added and the mixture cooled in ice. The deep red crystalline precipitate was filtered and washed with 80% alcohol and finally absolute alcohol. Yield: 1.6 g.; 94%.

Found: Os = 43.4%.

Calculated for $(\text{NH}_4)_2\text{OsCl}_6$: Os = 43.35%.

Ammonium Pentachlor-hydroxy Osmate IV.

A mixture of osmium tetroxide (1.0 g.), ferrous sulphate (5 g.), concentrated hydrochloric acid (3 ml.), sulphuric acid (10 N—4 ml.), ammonium chloride (0.5 g.) and water (15 ml.) was heated on the water bath in a stoppered flask for two hours. After standing overnight, a very small quantity of red crystals of ammonium hexachlorosmate had been deposited. After filtration the deep greenish red solution was treated fractionally with 20% ammonium chloride solution to give a greenish brown precipitate of the pentachlor-hydroxy salt. Finally the solution was treated with 2 g. of solid ammonium chloride and 10 ml. of concentrated hydrochloric acid and evaporated nearly to dryness. Sufficient water was added to dissolve the ferric salts and the mixture filtered to give a further crop of the substance. This was finally dissolved in the minimum volume of warm water and precipitated by the addition of ammonium chloride. The dark greenish brown crystals were washed with 90% alcohol. Yield: 0.5 g.; 30%.

Found: Os = 45.4%; Cl = 42.19%.

Calculated for $(\text{NH}_4)_2[\text{OsCl}_5\text{OH}]$: Os = 45.21%; Cl = 42.19%.

SUMMARY.

Ammonium hexachlorosmate was obtained in almost quantitative yield from osmium tetroxide by reduction with ferrous chloride and hydrochloric acid, followed by addition of ammonium chloride. Ammonium pentachlor-hydroxy osmate was obtained in a similar manner by using ferrous sulphate as the reducing agent.

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THE ESSENTIAL OILS OF *ZIERIA SMITHII* (ANDREWS) AND ITS VARIOUS FORMS.

PART II.

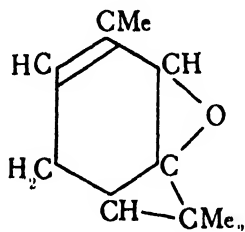
By F. R. MORRISON,
A. R. PENFOLD
and SIR JOHN SIMONSEN.

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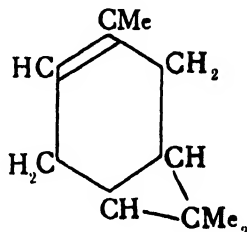
The results of examination of the essential oils of this small Rutaceous shrub, which occurs in moist situations throughout New South Wales, Victoria and Queensland, were first published in 1930 (Penfold, 1925). The oils proved to be a very remarkable series, rich in the phenol ethers, safrole, methyl eugenol and elemicin.

The variation in chemical composition, and the probable occurrence of physiological forms, made it desirable for publication at that date to be restricted to the results obtained with material growing in Queensland. These oils consisted mainly of safrole with some methyl eugenol. The investigation has been continued for over twenty-five years, but has only recently been completed.

One constituent of unusual interest was isolated from the essential oil obtained from plants collected in New South Wales. This substance, *l*- Δ^3 -carene-5 : 6-epoxide (I) was investigated by Penfold, Ramage and Simonsen (1939) and is closely related to *l*- Δ^3 -carene (II). It is thus the third substance containing the carane ring to be found in nature.



I



II

Carene-epoxide appears to be present in greatest amount in the plants collected from the Bellinger River district of New South Wales. This is evident from the *l*-avo-rotation of the crude oils distilled from that material.

Our botanical material was carefully examined by Mr. E. Cheel when Curator of the National Herbarium, Botanic Gardens, Sydney, in 1927. Although identified as *Zieria smithii*, Mr. Cheel expressed the opinion that the Bellinger River material differed sufficiently in morphological characters from the type to be considered a definite form. Pending agreement by botanists, we propose distinguishing the Bellinger River plant by naming it *Zieria smithii* variety "A". The present paper deals with the chemistry of the essential oils obtained from material collected in various parts of New South Wales.

The principal constituents so far identified are as follows, viz. :

Safrole, methyl eugenol, elemicin, *d*- α -pinene, *l*- Δ^3 -carene-5 : 6-epoxide, linalool and eugenol. An unidentified alcohol, $C_{10}H_{14}O$, and nopinone (?) are also present.

The phenol ethers occur singly or in admixture ; in some instances all three occur together as observed with the oils obtained from the Bellinger River and Lilyvale. The occurrence of the three phenol ethers, mentioned in varying proportions in the foliage from different localities, is of unusual interest. Although in some instances one particular phenol ether may predominate, namely safrole, methyl eugenol or elemicin, to the extent of 80 %-90 %, it is usually accompanied by a small quantity of one of its associates.

The yields of oil varied from 0.5 % to 1.2 %, calculated on the freshly cut leaves and terminal branchlets.

EXPERIMENTAL.

Three thousand five hundred and forty-eight pounds weight of leaves and terminal branchlets, collected in various parts of New South Wales, were subjected to steam distillation. The distillates were usually pale yellow oils, heavier than water, highly refractive, and they possessed the characteristic odour of the phenol ethers, modified by that of carene-epoxide.

It was practicable, in the course of distillation of the leaves, to separate the portion of oil lighter than water from the heavier-than-water fraction. This separation proved useful in isolating and identifying the lower boiling constituents. A typical example is given under the heading of *l*- Δ^3 -carene-5 : 6-epoxide in the appended table. Unless otherwise stated, the chemical and physical constants were taken on the mixed distillates.

It would be impracticable to record the results of examination of the oils from each consignment. For the purpose of this paper one or two are selected as typical examples.

The oil from a consignment of leaves collected at Toronto, New South Wales, on 27th January, 1925, was subjected to fractional distillation under reduced pressure, with the following results, viz. :

100 ml. crude oil taken.

| B.P./10 mm. | Volume. (Ml.) | $d_{15}^{15^{\circ}}$ | $n_D^{20^{\circ}}$ | $\alpha_D^{20^{\circ}}$ |
|------------------|------------------|-----------------------|--------------------|-------------------------|
| 50- 90° | 20 | 0.8677 | 1.4662 | +37.2° |
| 90-126° | 20 | 1.0027 | 1.5092 | -1° |
| 126-150° | 50 | 1.0652 | 1.5285 | -0.55° |
| Residue | 6 | | | |

On redistillation, the following fractions were finally obtained :

| B.P. | Volume. (Ml.) | $d_{15}^{15^{\circ}}$ | $n_D^{20^{\circ}}$ | $\alpha_D^{20^{\circ}}$ |
|---------------------|------------------|-----------------------|--------------------|-------------------------|
| 153-158°/766 mm. .. | 10 | 0.8596 | 1.4653 | +43.6° |
| 50-100°/ 10 mm. .. | 4 | 0.8829 | 1.4703 | +23.4° |
| 100-110°/ 10 mm. .. | 6 | 0.9640 | 1.4938 | -3.4° |
| 110-140°/ 10 mm. .. | 14 | 1.0479 | 1.5253 | -1.5° |
| 140-150°/ 10 mm. .. | 30 | 1.0650 | 1.5294 | $\pm 0^{\circ}$ |

TABLE 1.
Zieria muhlii (Andrews) from New South Wales.

| Date. | Locality in New South Wales. | Weight of Leaves. | Yield of Oil. | d_{15}^{15} | n_D^{20} | α_D^{20} | Solubility in 70% Alcohol. (W/W.) | Ester No. 14 Hours Hot Sap. | Ester No. after Acetylation. | Principal Constituents. | Remarks. |
|------------|--|-------------------|---------------|---------------|------------|-----------------|-----------------------------------|-----------------------------|------------------------------|---|--|
| 27/ 9/1923 | Terrigal (Official Collector). | Lb. 32½ | % 1.1 | 1.0382 | 1.5136 | +9.2° | Vol. 8.5 | 58.0 | 128.6 | Safole. | |
| 14/ 2/1924 | Narrabeen. | 4 | 1.2 | 1.0321 | 1.5273 | +0.85° | 1.0 | — | — | Methyl eugenol. | |
| 15/ 2/1924 | Terrigal. | 89 | 0.71 | 1.0407 | 1.5145 | +4.0° | 7.5 | — | — | Safole. | |
| 27/ 1/1925 | Toronto. | 135 | 0.67 | 1.0094 | 1.5102 | +6.0° | 1.0 | 5.5 | 36.48 | Elemicin and safole. | |
| 9/ 9/1925 | Condong (H. Johnson). | 76 | 0.45 | 1.022 | 1.5111 | +9.4° | 0.9 | 36.5 | 89.00 | Safole and methyl eugenol. | |
| 12/ 7/1926 | Bellinger River (A. J. Washington). | 39 | 1.57 | 1.0085 | 1.5084 | -18.1° | 0.9 | 81.5 | 106.00 | Methyl eugenol and elemicin. | Variety "A". |
| 7/ 3/1927 | Bellinger River (A. J. Washington). | 77 | 1.06 | 1.011 | 1.5084 | -11° | 1.0 | 78.2 | 107.2 | Methyl eugenol and elemicin. | Variety "A". |
| 12/ 8/1927 | Bellinger River (A. J. Washington). | 53 | 1.6 | 1.0122 | 1.5083 | -8.4° | 1.0 | 77.2 | 105.00 | Methyl eugenol and elemicin. | Variety "A" in full flower. |
| 16/ 7/1930 | Bellinger River (W. P. Tyson). | 130 | 0.80 | 1.0136 | 1.5100 | -4.25° | 0.8 | — | 104.4 | | Identified by E. Cheel as a form of the type (var. "A"). |
| 18/ 8/1930 | Bellinger River (F. Gale). | 160 | 0.38 | 0.9863 | 1.4950 | -29.8° | 0.9 | 158.3 | 172.0 | | Portion lighter than water. |
| 29/10/1934 | Bellinger River (W. P. Tyson). | 215 | 0.68 | 1.0187 | 1.5135 | -3.8° | 0.9 | 53.1 | 71.6 | | Portion heavier than water (var. "A"). |
| 16/ 6/1936 | Bellinger River (W. P. Tyson). | 1438½ | 1.29 | 0.9978 | 1.5022 | -3.2° | 0.9 | 100.0 | 115.8 | | Variety "A". |
| 31/ 8/1936 | Bellinger River (W. P. Tyson). | 1010 | 1.4 | 0.9896 | 1.4996 | -5.0° | 0.9 | 97.4 | 150.2 | Safole, methyl eugenol and elemicin. | Variety "A". |
| 19/ 8/1947 | Condong (Colonial Sugar Refining Co.). | 80 | 1.18 | 0.9857 | 1.4981 | +0.6° | 1.0 | 105.2 | 149.1 | | In full flower (var. "A"). |
| 8/ 9/1947 | Newport, near Sydney. | 27 | 0.47 | 1.012 | 1.5120 | -0.92° | 10.0 | 41.4 | 61.6 | Safole and methyl eugenol. | |
| 14/ 7/1949 | Narrabeen, near Sydney | 64 | 0.9 | 1.005 | 1.5076 | +7.25° | 1.5 | 36.0 | 69.0 | Safole, methyl eugenol and elemicin. | |
| 21/ 7/1949 | Palm Beach. | 27 | 0.73 | 1.025 | 1.5220 | +2.75° | 3.0 | — | — | Safole, methyl eugenol and elemicin. | |
| 18/ 8/1949 | Lilyvale. | 81 | 0.59 | 1.007 | 1.5198 | -1.90° | 0.7 | — | — | Methyl eugenol. | |
| | | | 0.21 | 1.017 | 1.5221 | -0.65° | 1.0 | 22.3 | 36.1 | Methyl eugenol (80%), safole (under 10%). | |

Determination of d- α -pinene.

2 Ml. of the fraction distilling at 153–158°/766 mm. on mixing with an equal volume of *l*- α -pinene gave an excellent yield of pinene nitrosochloride, m.p. 109°, raised by recrystallization to 115°. 8 ml. on oxidation with potassium permanganate (Penfold, 1922a), yielded pinonic acid m.p. 69–70° [α]_D²⁰ = +90.1° (in CHCl₃, C=3.3) The semicarbazone of the acid had m.p. 208°.

Determination of Safrole.

The fractions distilling at 100–110° and 110–140°/10 mm. were mixed together and placed in a bath of solid carbon dioxide; the frozen mass was transferred to a Buchner filter funnel surrounded by a mixture of ice and salt. By continued repetition of this process the principal constituent, safrole, was separated, and purified by fractional distillation. It possessed the following physical and chemical characters: b.p. 230–233°/762 mm., m.p. 11°, d_{15}^{15} 1.1046, n_D^{20} 1.5375, α_D^{20} –0.2°.

10 g. of the safrole were oxidized with potassium permanganate in accordance with the method described (Penfold, 1925, p. 87) and gave a good yield of piperonylic acid m.p. 228°, both alone and in admixture with an authentic specimen.

Determination of Elemicin.

The fraction distilling between 140° and 150°/10 mm. was oxidized with potassium permanganate in alkaline solution in accordance with the procedure described by Penfold (1922b). Two acids were obtained, trimethyl gallic, m.p. 169–170°, and trimethyl-homogallic, m.p. 119–120°, which placed the identity of the phenol ether as elemicin beyond doubt. Mixed melting points showed no depression.

Leaves Collected at Terrigal, New South Wales.

Oil from a consignment of leaves collected at Terrigal on 15th February, 1924, was subjected to fractional distillation under reduced pressure, with the following results, viz.:

100 ml. of crude oil, after removal of all alkali-soluble substances with 8% sodium hydroxide solution, gave the following results on distillation:

| B.P. | Volume. (Ml.) | d_{15}^{15} | n_D^{20} | α_D^{20} |
|-----------------------|------------------|---------------|------------|-----------------|
| 50–60°/10 mm. | 7 | 0.8635 | 1.4664 | +39.45° |
| 60–105°/10 mm. | 8 | 0.9488 | 1.4865 | +21.5° |
| 105.5–109°/10 mm. .. | 26 | 1.0495 | 1.5140 | +7.5° |
| 109.5–112°/4–5 mm. .. | 45 | 1.0815 | 1.5261 | +3.7° |
| Residue | 14 | — | — | — |

Determination of d- α -pinene.

Similar results were obtained with the first fraction as in the examination of the oil from Toronto, 27th January, 1925.

Determination of Safrole.

Safrole was separated from the second and third fractions by the method described above, and had m.p. 11°, d_{15}^{15} 1.1031, n_D^{25} 1.5339, α_D +0.85°. It was converted to isosafrole by treatment with sodium ethoxide in ethyl alcohol. The isosafrole subsequently isolated possessed the following constants: b.p. 120.5–122°/10 mm., d_{15}^{15} 1.123, n_D^{20} 1.5740. It was oxidized with chromic acid in glacial acetic acid solution to piperonal. The crude aldehyde was purified through the bisulphite compound, and, on recrystallization from ethyl alcohol, had m.p. 37°, both alone and in admixture with an authentic sample.

Determination of Nopinone (?).

The first fraction, after washing with 50% resorcin solution, yielded 1 ml. of oil having $n_D^{14.5}$ 1.4760. It was converted to the semicarbazone, which, after recrystallization from ethyl alcohol, had m.p. 189–190°, both alone and in admixture with an authentic sample.

Found: C, 61.46; H, 9.07. $C_{10}H_{17}ON_3$ requires: C, 61.53; H, 8.7.

The identity of this ketone requires confirmation, since it has not previously been found to occur in nature. The rapid extermination of this plant in settled areas makes further collection difficult.

Determination of Linalool and Unidentified Alcohol, $C_{10}H_{14}O$.

The presence of a small percentage of linalool in this oil was established by the preparation of the xenyl urethane m.p. 83–85°, both alone and in admixture with an authentic example (Penfold, Ramage and Simonsen, 1939).

An unidentified alcohol was characterized by the preparation of its 3:5-dinitrobenzoate, m.p. 119° (Penfold, Ramage and Simonsen, 1939).

Minor Constituents.

Eugenol, to the extent of 2% of the crude oil, was isolated from the alkali-soluble substances in the usual way, and the benzoate prepared. It had m.p. 69–70°, both alone and in admixture with an authentic sample.

Volatile Acids—Acetic and Citronellic (?).

Small amounts of volatile acids, both free and combined, were isolated after saponification of the oil. Silver salt of water-soluble acid gave 63.8% Ag. $C_4H_7O_2Ag$ requires 64.67% Ag. A volatile oily acid was obtained, the silver salt of which gave 38.52% Ag. $C_{10}H_{18}O_2Ag$ requires 38.99% Ag.

Determination of l - Δ^3 -carene-5:6-epoxide.

This substance was found to occur in the oils obtained from the leaves and terminal branchlets collected from the Bellinger River district of New South Wales; it is the principal constituent of the fraction boiling below 100°/10 mm.

The fraction of boiling point 88–90°/17 mm., on digestion with alkali, or if heated with water at 150°, gave geranic acid practically in quantitative yield. After removal of impurities such as linalool and the unidentified alcohol $C_{10}H_{14}O$, referred to above, the oil gave figures on analysis in close agreement with those required for $C_{10}H_{14}O$. This substance was l - Δ^3 -carene-5:6-epoxide, a colourless sweet smelling oil having the constants, b.p. 83–85°/14 mm., d_{25}^{25} 0.9454, n_D^{25} 1.4729, $[\alpha]_{5461}^{25}$ –88°. Its structure and properties have been discussed elsewhere (Penfold, Ramage and Simonsen (1939); Penfold and Simonsen (1942)).

Leaves Collected at Fernmount, Bellinger River, 12th July, 1926. Determination of Methyl Eugenol.

The crude oil, on distillation, yielded a fraction possessing the following constants:

B.p. 130–135°/10 mm., d_{15}^{15} 1.0435, n_D^{20} 1.5274, α_D^{20} 1.5°.

6 Ml. on oxidation with potassium permanganate (Penfold, 1925) gave an excellent yield of veratric acid m.p. 179–180°, unaltered in admixture with an authentic specimen.

* Fractions boiling from 135–147°/10 mm. were found to consist principally of elemicin. Oxidation with potassium permanganate in alkaline solution gave trimethyl gallic acid, m.p. 169–170°, and trimethyl-homogallic acid, m.p. 119 to 120°. Mixed melting points showed no depression.

The presence of saffrole was not detected in this sample of oil.

SUMMARY.

The essential oils of *Zieria smithii*, a Rutaceous shrub found growing in moist situations throughout Queensland, New South Wales and Victoria, consist principally of one or more of the phenol ethers, safrole, methyl eugenol and elemicin. The oils obtained from plants growing in New South Wales contain also *d*- α -pinene, *l*- Δ^3 -carene-5 : 6-epoxide, linalool, an unidentified alcohol $C_{10}H_{14}O$, and nopinone (?). The chemistry of the latter oils is described in this paper.

ACKNOWLEDGEMENTS.

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